SULFUR DIOXIDE--ITS CHEMISTRY AND REMOVAL FROM INDUSTRIAL WASTE GASES

By D. Bienstock, L. W. Brunn, E. M. Murphy,
and H. E. Benson

• • • • • • • • • **Information Circular 7836**

UNITED STATES DEPARTMENT OF THE INTERIOR
Fred A. Seaton, Secretary
BUREAU OF MINES
Marling J. Ankeny, Director

1958

CONTENTS

Page

Summary and introduction 1
Acknowledgments 2
Absorption of sulfur dioxide 2
    Mechanism of sulfur dioxide absorption and regeneration ... 3
    Absorption processes for flue gases of low-sulfur dioxide concentration 3
        Effluent processes 3
            Use of manganese ion as catalyst 4
            Battersea process 4
        Noneffluent (cyclic) processes 5
            Use of lime (Howden-I.C.I. process) 5
            Ammoniacal solutions 7
            Sodium sulfite-bisulfite system 8
    Absorption processes for gases of high sulfur dioxide concentration 10
        Basic aluminum sulfate process - I.C.I. 10
        Use of amines 11
        Magnesium hydroxide 12
Adsorption of sulfur dioxide 13
    Adsorption of mixed vapors 15
    Adsorption on carbon 15
    Adsorption on silica gel 16
    Adsorption on platinum 16
    Adsorption on oxides of chromium 18
    Adsorption on oxides of iron 19
    Adsorption on oxides of vanadium 19
Reaction of sulfur dioxide with metals and metallic oxides 20
    Reaction with metals 20
        Copper 20
        Iron 20
        Magnesium 21
        Nickel 21
    Reaction with metallic oxides 22
        Aluminum oxide 22
        Calcium oxide 22
        Oxides of copper 22
        Oxides of chromium 23
        Oxides of iron 23

CONTENTS (Con.)

Page

- Oxides of lead 23
- Oxides of manganese 24
  - Industrial applications 25
    - Manganese Ore Co. process 25
    - Bureau of Mines proposed dithionate process. 26
- Oxides of tin 26
- Reduction of sulfur dioxide with gases 27
  - Reaction with hydrogen 27
  - Reaction with hydrogen sulfide 28
  - Reaction with carbon monoxide 29
    - Bolidens process 30
    - Trail process 30
  - Reaction with methane 31
    - Commercial processes employing methane or hydrocarbon gases in reducing sulfur dioxide 32
      - Thiogen processes 32
        - Dry process 32
        - Wet process 33
      - Asarco process 33
- Reduction of sulfur dioxide with carbon 35
  - Formation of sulfur 35
  - Formation of carbon disulfide 36
- Oxidation of sulfur dioxide 38
  - Use of air 38
    - Contact process 39
  - Use of ozone 40
- Effect of heat on sulfur dioxide 41
- Effect of light on sulfur dioxide 41
  - Dissociation of sulfur dioxide 41
  - Oxidation of sulfur dioxide 42
- Effect of an electric discharge on sulfur dioxide 42
  - Technical applications in using electric discharge 42
- Decomposition of sulfates 43
  - Thermal dissociation 43
  - Electrolysis of metal sulfates 45
  - Hydrogen reduction of sulfates 45
- Electrolysis of compounds containing sulfur 46
  - Electrolytic oxidation of sulfides 46
  - Oxidation of sulfurous to sulfuric acid 47
  - Electrolytic oxidation of thiosulfates 47
  - Electrolytic oxidation of sulfites 48
  - Electrolysis of sulfates 48
    - Electrolysis of sulfuric acid 48
    - Electrolysis of metal sulfates 48
  - Electrolytic reduction of bisulfites 50
- Sulfur - production and uses 51

CONTENTS (Con.)

Page

Possible methods for preventing atmospheric contamination by sulfur dioxide 52
  - Reduction of sulfur in coal before combustion 53
    - Mechanical cleaning of coal 53
    - Partial gasification of coal 54
      - Low-temperature carbonization 55
      - Carbonization in the presence of various gases .. 56
    - Complete gasification of coal 56
      - Coal, oxygen, and steam 56
      - Producer gas 57
  - Removal of sulfur dioxide in flue gas after combustion 57
    - Solid-phase reactions 58
      - Absorption with lime 58
      - Absorption with oxides of manganese 59
      - Absorption with lead dioxide 60
      - Absorption with cupric oxide 61
      - Reaction with a "fouled" Huff catalyst 62
      - Adsorption with an impregnated charcoal 62
    - Gas-phase reactions 62
      - Catalytic reduction with hydrogen sulfide 62
      - Reactions induced photochemically or by electric discharge 63

Conclusions 63

Physical properties of sulfur dioxide 64
  - Boiling point 64
  - Coefficient of expansion 64
  - Critical constants 66
  - Density 66
  - Dielectric constant 67
  - Electrical conductivity 68
  - Enthalpy and entropy 68
  - Free energy of formation 68
  - Heat capacity 68
  - Heat of formation 71
  - Heat of fusion 72
  - Heat of vaporization 72
  - Magnetic susceptibility 72
  - Molecular weight 73
  - Melting point 73
  - Refractivity 73
  - Solubility in water 73
  - Specific gravity 74
  - Surface tension 74
  - Thermal conductivity 74
  - Thermodynamic functions 75
  - Vapor pressure 76

CONTENTS (Con.)

Page

Vapor pressure of aqueous solutions 76
Viscosity 76
Abbreviations of journal references 79
Bibliography 81

ILLUSTRATIONS

Fig.

1. Battersea process 5
2. Howden-I.C.I. cyclic lime process 6
3. Flowsheet of present sulfur dioxide recovery operations at Trail, B. C. 8
4. Fulham Simon-Carves ammoniacal-liquid process 9
5. Johnstone and Singh zinc oxide process 10
6. Fleming and Fitt dimethylaniline process 12
7. Typical adsorption curves for charcoal 14
8. Adsorption of SO_2 in cc./gm. of gel at 0°, 30°, and 100° C. 17
9. Adsorption isotherms of sulfur dioxide on platinum black.. 18
10. Simplified flow diagram of Asarco process 34
11. Flowsheet of Monsanto contact acid plant 40
12. Potential of 1 and 10^{-3} molar metal solutions, and hydrogen potential at varying pH (25° C.) 46
13. Consumption of sulfur from all sources, by industries in the United States 1952-55 average 51
14. Bureau of Mines low-temperature-carbonization process 55

TABLES

1. Hydrogen reduction of various nickel solutions 45
2. Values of principal forms of sulfur 52
3. Reduction in total sulfur and pyritic sulfur obtained in cleaning tests, compared with percentage of fine pyritic and organic sulfur in raw coal, percent 54
4. Properties of saturated sulfur dioxide 65
5. Properties of superheated sulfur dioxide 69
6. Partial pressures of water and sulfur dioxide over aqueous solutions of sulfur dioxide 77

SULFUR DIOXIDE-ITS CHEMISTRY AND REMOVAL FROM INDUSTRIAL WASTE GASES[1]

by

D. Bienstock,[2] L. W. Brunn,[2] E. M. Murphy,[2]
and H. E. Benson[3]

SUMMARY AND INTRODUCTION

Contamination of the atmosphere by sulfur dioxide, whether in dilute concentrations of 0.05 to 0.3 volume-percent (such as in the flue gases of powerplants) or as much as 5 to 10 percent (as in the roaster gases of smelter plants) (40, 166)[4] long has been a public health problem. The interest shown by the Government and industry has intensified in recent years. The technical literature on air pollution is rapidly growing (30, 135, 137, 140, 143, 146).

The Bureau of Mines and the United States Public Health Service are participating in a project for developing processes that remove sulfur dioxide from gaseous effluents or minimize their noxious and toxic properties.

One part of this report is a compilation of published information on the chemistry of sulfur dioxide, emphasizing reactions having current and potential application to the problem of air pollution. This report was prepared to serve as an annotated bibliography to orient the early thinking of personnel engaged on the project. Appraisal of this and other information is now in progress. The literature will be searched further to support the experimental phase of the effort rather than add to the general descriptive material.

In commercial methods for removing sulfur dioxide from powerplant flue gases, gas-liquid contact is employed almost exclusively. The major absorption processes developed or in the pilot-plant stage are discussed. Processes for removing sulfur dioxide, when present in considerably greater concentrations, as in smelter off-gases, are also explained.

Adsorption techniques for removing injurious and harmful gaseous contaminants are well known. However, the adsorption generally takes place at relatively low temperatures. Adsorption at flue-gas temperatures offers an interesting approach. The literature on potential adsorbents has been reviewed with this in mind.

Absorption with liquids results in a cooling of the partly scrubbed gas. The latter loses its buoyancy and may hover at ground level near the stack, enhancing rather than removing the local pollution problem. Reaction with hot metal or metal oxide would allow the scrubbed gas to be discharged while still hot and readily dissipated into the upper atmosphere.

---

[1] Work on manuscript completed May 1957.

[2] Chemical engineer, Region V, Bureau of Mines, Bruceton, Pa.

[3] Former chief, Gas-Synthesis Section, Bureau of Mines, Bruceton, Pa.

[4] Underlined numbers in parentheses refer to items in the bibliography at the end of this report.

Processes involving the reduction of sulfur dioxide with reducing gases or with carbon are well known. These processes, however, have been adapted to high concentrations of sulfur dioxide; modifications to allow removal of sulfur dioxide in low concentration are a strong possibility.

Oxidation of sulfur dioxide is discussed. A more active catalyst than is now employed in the contact process would be necessary to operate at the lower temperatures available with a flue gas.

Physical methods, such as the use of ultraviolet radiation and high-voltage electric discharge, are then examined. Although these methods are well covered in the patent literature, they have not been exploited enough.

Because of the economic necessity of having a process that is regenerative, methods of recovering the spent absorbent, such as electrolysis and thermal dissociation, are covered.

In the remainder of the report, the authors suggest alternative methods of reducing pollution. By lowering the sulfur concentration in the coal before combustion by coal cleaning and partial gasification, reduction in the sulfur dioxide content upon combustion will be accomplished. Some of the gas-solid absorption processes being considered by the Bureau of Mines are reviewed.

An extensive summation of the physical properties of sulfur dioxide is given for the convenience of those working in this field.

ACKNOWLEDGMENTS

Acknowledgment is made to the following organizations for permission to reproduce the several figures given in the report: McGraw-Hill Publishing Co., Inc., The American Institute of Mining, Metallurgical, and Petroleum Engineers, The American Chemical Society, The American Society of Mechanical Engineers, The American Mining Congress, and the Reinhold Publishing Corp.

Sincere appreciation is expressed for the critical reviews and the many suggestions offered by Bureau personnel.

ABSORPTION OF SULFUR DIOXIDE

More progress has been made in removing sulfur dioxide from flue gases by gas-washing processes than by other techniques. Despite the limited success there are many almost insurmountable difficulties. Rees (180) enumerates some of the problems involved:

(1) A minimum removal of 90 percent of the sulfur dioxide from gas flows of more than 1 million cubic feet per minute is required. Less effective removal would be nullified, as far as ground-level pollution is concerned, by the inevitable loss in buoyancy of the scrubbed gas owing to cooling.

(2) Presence of other components in the flue gas such as oxygen and hydrogen chloride may lead to undesirable and wasteful side reactions.

(3) Because of its magnitude, disposal of the end product, whether salable or waste, is a serious problem.

(4) The possible need for a spare gas-washing plant to prevent interruption of electrical generation.

Mechanism of Sulfur Dioxide Absorption and Regeneration (2)

When an acid gas like sulfur dioxide dissolves in water, the gas is in equilibrium with the ions formed. Thus $(H^+)^2 \cdot (SO_3^=) = k \cdot P_{SO_2}$, and the capacity of an aqueous liquid to dissolve sulfur dioxide at any gas pressure is inversely proportional to the square of the hydrogen-ion concentration.

The solution of sulfur dioxide in water gives rise to a rapid increase in hydrogen-ion concentration; consequently, solution soon stops. If alkalis are present and the rise in H^+ is prevented, large quantities can be dissolved, but H^+ is now too low to allow regeneration on rise of temperature. A good solvent for sulfur dioxide must be one that is buffered in such a way that large quantities of sulfur dioxide can be dissolved without appreciable rise of H^+. Satisfactory reversible absorption can only occur with aqueous solvents heavily buffered at a pH close to 3.5. More acid solutions will have a poor affinity for sulfur dioxide; more alkaline solutions will not regenerate easily and will tend to dissolve other gases such as carbon dioxide, which may be present. The basic aluminum sulfate process, which is discussed on p. 10, was developed utilizing a solution having the required buffer effect.

The mechanism of sulfur dioxide absorption, interpreted in the light of the two-film theory, is discussed for several alkaline mediums - sodium carbonate, sodium bicarbonate, and sodium sulfite. For the first alkali, the resistance is essentially all in the gas film; for the last two the controlling resistance shifts toward the liquid film (237).

Absorption Processes for Flue Gases of Low Sulfur Dioxide Concentration

The following processes have been developed to reduce the low concentration of sulfur dioxide in flue gases to acceptable limits. These processes are divided into two classes - (1) the effluent processes in which no attempt is made to recover the solvent and (2) the noneffluent or cyclic processes in which the absorbent liquid is recirculated after regeneration.

Effluent Processes

The principal liquid solvent is water; however, scrubbing with water is expensive because of the low solubility of sulfur dioxide and the necessity of using large quantities of water.

$$SO_2 \text{ Gas} + H_2O \rightleftharpoons SO_2 \text{ Sol.} + H_2O \rightleftharpoons H_2SO_3 \overset{K_1}{\rightleftharpoons} H^+ + HSO_3^-, \text{ and } HSO_3^- \overset{K_2}{\rightleftharpoons} H^+ + SO_3^=.$$

Approximately 11 tons of water at 68° F. (205) is the theoretical minimum for recovering 85 percent of the sulfur dioxide from a gas produced from the combustion of 1 ton of coal containing 1 percent sulfur. Furthermore, the low driving force available, the difference between the partial pressure in the gas and the equilibrium pressure above the solution, and the large liquid-and-gas-flow rates make it necessary, in commercial practice, to employ an absorption apparatus having a large volume and enormous quantities of water.

Johnstone, (105) in scrubbing sulfur dioxide from flue gases with industrially available water, noted that the apparent solubility was greater than indicated from the equilibrium values of sulfur dioxide with pure water. This excess solubility indicated a secondary reaction taking place after the gas dissolved - interaction with alkaline impurities or with dissolved oxygen, the latter to form sulfuric acid. The effect of this secondary oxidation was more striking when hot water (145° F.) was employed for scrubbing.

Use of Manganese Ion as Catalyst

Johnstone (104) found that some metallic ions act as catalysts for absorbing sulfur dioxide by water. Manganese (manganese sulfate), in concentrations as low as 0.0028 percent, increased the solubility of sulfur dioxide in water by 600 percent. When a mixture of sulfur dioxide in air was bubbled through water containing manganese ion as catalyst, sulfuric acid was produced. For a concentration of 0.03-percent-manganese ion, a 30-percent sulfuric acid concentration was obtained.

Copson and Payne (32) studied the reaction further and were able to obtain higher rates of absorption. The rate of absorption decreased as the acid concentration increased. Thirty-percent acid is readily produced, but the production of sulfuric acid ceases at a concentration of 40 percent.

When water that contained 0.003 percent manganese as $MnSO_4$ was used for scrubbing, impurities such as phenol, cresol, and xylenol acted as inhibitors at concentrations as low as 0.005 percent; polyhydric phenols, catechol, resorcinol, and pyrogallol stopped the oxidation completely (183).

Use of ozone to maintain the rate of oxidation of sulfur dioxide with air in presence of manganese ion (89) is the basis of recent pilot-plant work at TVA (219). A small quantity of ozone was added to the flue gas, and the mixture was scrubbed with a dilute solution of sulfuric acid containing manganese ion. The maximum concentration of sulfuric acid recovered was 40 percent. A simulated flue gas containing 0.35 percent sulfur dioxide, to which was added 240 parts per million of ozone, was scrubbed with an acid containing 0.3 percent manganese. Ninety-five percent of the sulfur dioxide was removed. Further concentration of the acid by means of the sensible heat in the flue gas between 150° and 55° C. was suggested.

Battersea Process

Since 1935 the London Power Co. (94) gas-washing plant at the coal-fired Battersea Power Station has used the water of the Thames River, to which a small quantity of chalk has been added (fig. 1). The Thames River already contains most of the alkali (calcium bicarbonate) required to neutralize the sulfur dioxide and supplies the water that carries away the product calcium sulfate in solution. Some manganese sulfate is also added to the effluent to activate oxidation of sulfite in the aeration tank. This method is possible only on a comparatively large river, which is already so polluted that there is no risk of interfering with fishing or other riparian rights. The efficiency of this method is about 92 to 97 percent, and about 35 tons of water per ton of 1.0-percent sulfur-bearing coal is required. A major part of this water is required to keep the calcium sulfate in solution. The same process is to be installed at Bankside Power Station for scrubbing the flue gases that result from burning high-sulfur-content fuel oil (146).

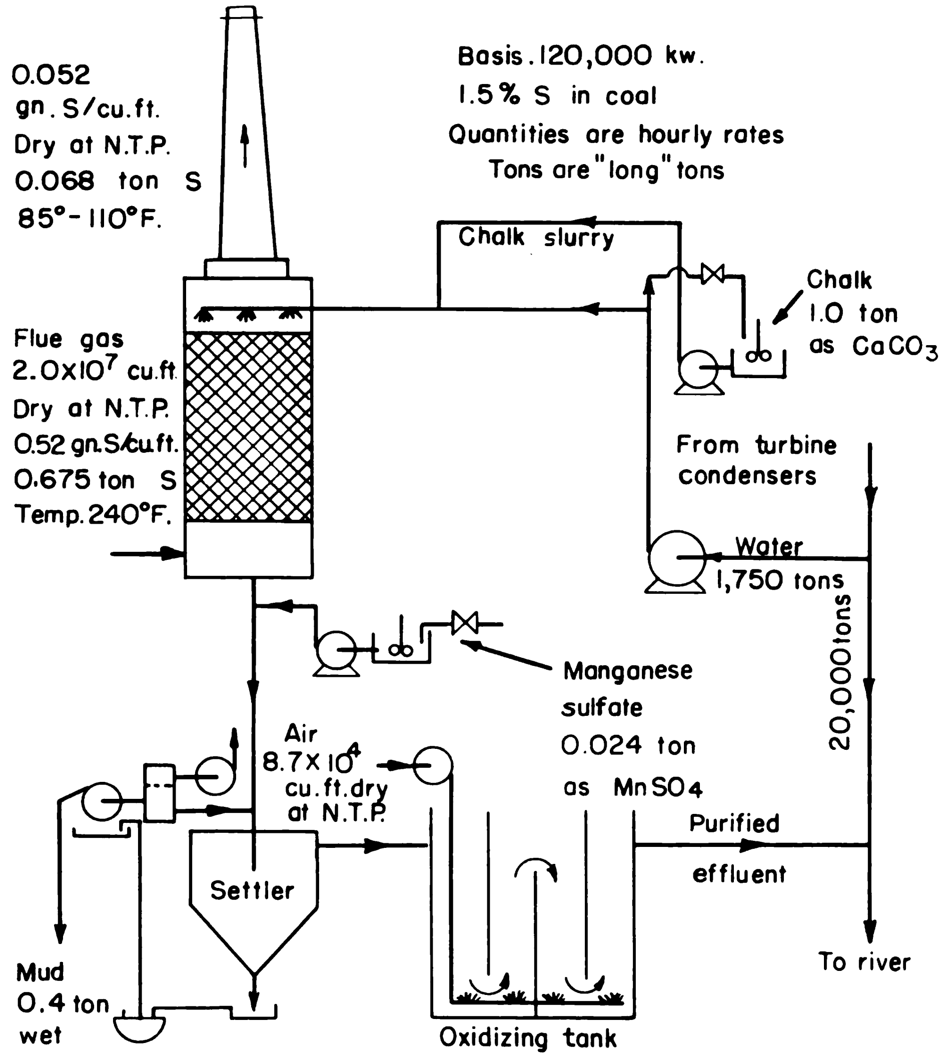


FIGURE 1. - Battersea Process. *(Reproduced From Rees, R. L. (180).)*

The principal defects of this process are the high cost of maintenance, the extent to which it cools the gas, and the strict limitation on the sites at which it can be used.

Noneffluent (Cyclic) Processes

Use of Lime (Howden-I.C.I. Process)

Because the effluent (noncyclic) process can be used only near a large river or sea, where there is enough water to carry away the effluent, a noneffluent (cyclic) process would find much greater usage. The only full-scale cyclic process is the lime process developed by J. Howden & Co. (163, 170) (see fig. 2). This process employs a lime or chalk slurry (5 to 10 percent) circulated through wooden grid-packed towers. Part of the circulating liquid is continuously withdrawn, the sludge is settled out, and the clarified liquid is returned to the system. Because of contamination by dust and grit in the gas, the sludge, principally calcium sulfate, is valueless; disposal thus presents a serious problem. Conversion of the calcium

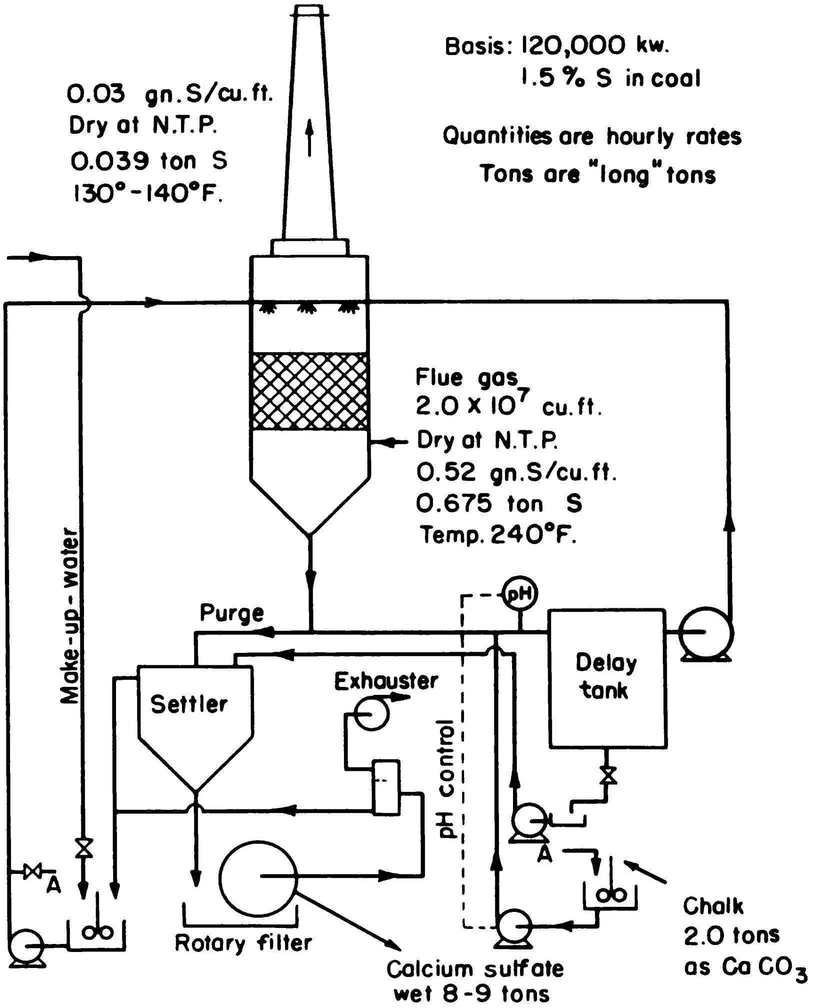


FIGURE 2. - Howden-I. C. I. Cyclic Lime Process. *(Reproduced From Rees, R. L. (180).)*

sulfate in the sludge to ammonium sulfate by digestion with ammonium carbonate (the latter produced in large quantities as a byproduct of the gas and coke-oven industries) would produce a salable product (62).

The process was first installed commercially at Tir John, Swansea, Wales. Various difficulties were encountered, and the plant was eventually dismantled. A plant that was installed at the Fulham Power Station, London, worked for several years and removed over 98 percent of the sulfur dioxide from the flue gases. The plant was shut down during World War II (180) and was not reopened, owing to the estimated high capital cost of renewing the plant.

The Howden process operated at Swansea was more than 99 percent effective in removing sulfur dioxide from flue gases, for example:

	Concentration, mg./liter		Elimination, percent
	In	Out	
Swansea plant	0.64	0.0018	99.7
Pilot plant	1.87	.0033	99.8

Original from THE OHIO STATE UNIVERSITY

Ammoniacal Solutions

Another noneffluent process employs an ammonia solution instead of lime to recover the sulfur directly in more useful forms, principally as ammonium sulfate, sulfur dioxide, or elemental sulfur. The concentration of sulfur dioxide in the exit gas may be reduced to as low as 0.0005 volume-percent, corresponding to removing 99 percent of the sulfur dioxide in the flue gas (36). If pure ammonia is used, the scrubbing liquor contains ammonium sulfate, sulfite, and bisulfite. If crude ammonia (concentrated gas-works ammoniacal liquor) is used, ammonium thiosulfate is also formed (114).

The spent liquor can be regenerated either by steam stripping or by a chemical method (106). When steam stripping is employed, the minimum ratio of steam to sulfur dioxide above the spent solution cannot be less than the molar ratio of water vapor to sulfur dioxide at the wet-bulb temperature of the original gases. The reason for this is that the molar latent heats of water and sulfur dioxide are approximately the same. Consequently, the effect of temperature on the vapor pressures of these constituents will be the same. Thus, if the solution comes approximately to equilibrium with the water vapor and sulfur dioxide in the original gases, the ratio of vapor pressures will remain approximately constant as the temperature is raised. Therefore, the steam requirements are necessarily high for recovering sulfur dioxide from waste gases containing large quantities of water vapor. Suggestions for improving steam regeneration, for the most part, are based upon adding a compound that gives a higher acidity to the ammonia solution when the solution is heated (107).

Chemical regeneration appears to be more economical. This type of regeneration has been used by the zinc-producing works of the Consolidated Mining & Smelting Co. of Canada, Ltd., Trail, B. C. (117) (see fig. 3), and by the National Smelting Co., Ltd., Avonmouth, England (234). Part of the solution is drawn off and treated with sulfuric acid to give ammonium sulfate and sulfur dioxide gas. Ammonia is added to the recycle solution to make up for the part converted into ammonium sulfate; part of the recovered gas is converted into the sulfuric acid consumed in the process.

Another method of chemical regeneration similar to the Katasulf process (5) has been proposed in the Fulham Simon-Carves ammoniacal liquor process and tested by the British on a pilot-plant scale (162, 210). Ammonium sulfate and free sulfur are produced by adding a small quantity of sulfuric acid to the bleed stream of the spent solution and heating this mixture in an autoclave under 200 p.s.i.g. pressure to a temperature of about 180° C. (see fig. 4). The reaction is believed to be (243):

$$2NH_4HSO_3 + (NH_4)_2S_2O_3 = 2(NH_4)_2SO_4 + H_2O + 2S.$$

Despite the effectiveness of this ammoniacal-liquor scrubbing process, its application will probably be limited by the supply of ammonia liquor and the sale of ammonium sulfate (54).

An interesting method of chemical regeneration in which the ammonia is recovered for further absorption was described in a recent patent (97). The ammonium bisulfite solution formed in the absorption is treated with a hot-acid solution of potassium-hydrogen fluoride to evolve sulfur dioxide. The resultant solution of potassium fluoride and ammonium fluoride is then evaporated to evolve ammonia, which is used for scrubbing more sulfur dioxide. The concentrated potassium-hydrogen fluoride solution formed in the evaporation step is used in the regenerative step.

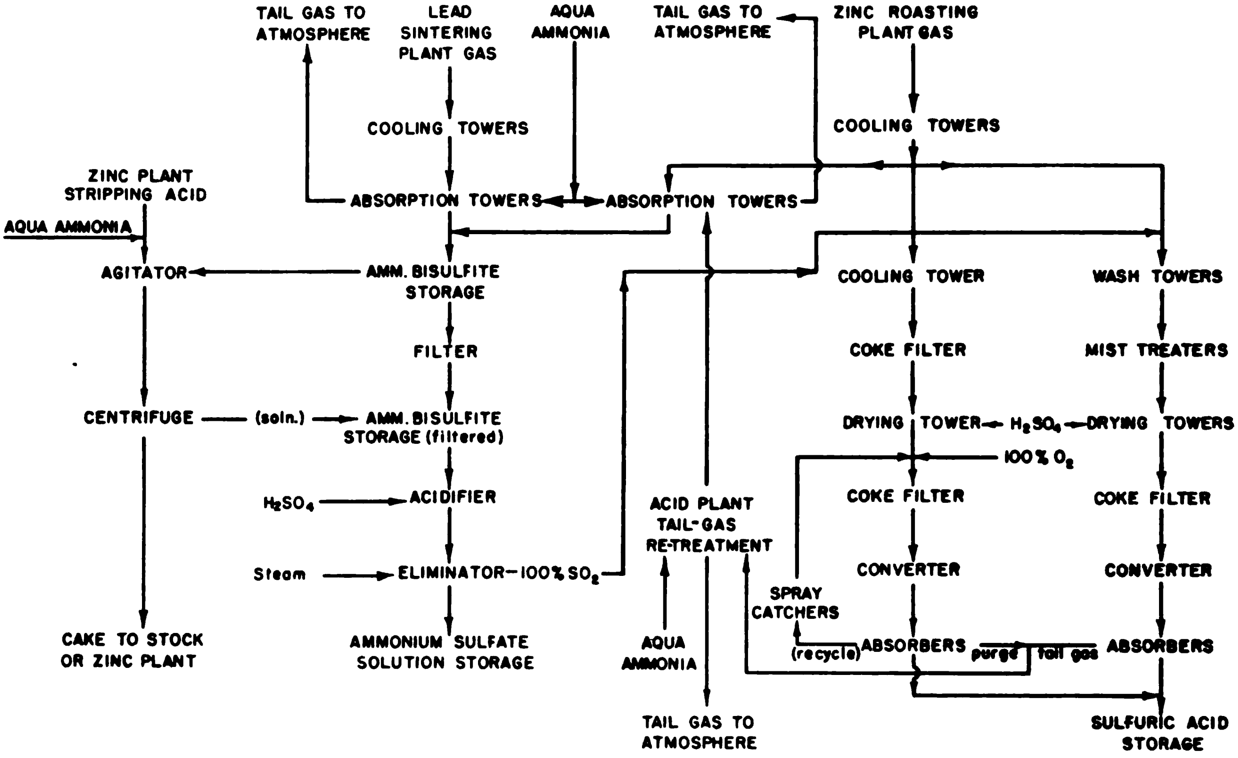


FIGURE 3. - Flowsheet of Present Sulfur Dioxide Recovery Operations at Trail, B. C.
(Reproduced From King, R. A. (117).)

Sodium Sulfite-Bisulfite System

In this method, capacity for absorbing sulfur dioxide is limited by the low solubility of the sulfites; nevertheless, the capacity of this dilute solution is many times that of water. Because of the nonvolatility of the base, steam regeneration may be carried further than that with ammonia solutions, and consequently sulfur dioxide may be recovered more completely, but considerably more steam is required. The addition of zinc oxide (108) to the spent solution permitted a greater degree of regeneration than was possible by the use of steam alone (fig. 5). The zinc oxide reacts with the bisulfite, giving insoluble zinc sulfite crystals, which are filtered off, dried, milled, and calcined in a flash calciner from which a gas containing 70 percent water and 30 percent sulfur dioxide is driven off. The gas is cooled, dried, and liquefied. The filtrate separated from the zinc sulfite slurry constitutes the regenerated liquor and is pumped back to the absorber for further sulfur dioxide removal. The calcined zinc oxide is returned to the clarified spent solution. The reaction is represented as

$$ZnO + NaHSO_3 + 2.5H_2O \rightarrow ZnSO_3 \cdot 2.5H_2O + NaOH,$$

$$NaOH + NaHSO_3 \rightarrow Na_2SO_3 + H_2O.$$

Difficulties are introduced by the formation of sulfate either by absorption of sulfuric acid vapor or by oxidation in any part of the cycle. The overall oxidation of sulfite to sulfate is about 10 percent. Accumulation of dissolved sulfate cannot be tolerated, because the absorptive capacity of the liquor is reduced. Therefore, a desulfating system is employed to remove sulfate ions. Enough sulfate is fed to the desulfating system by the underflow system from the clarifier so that the sulfate concentration is held at a low level in the absorber liquor.

The clarifier underflow, which contains ash and calcium sulfite crystals, passes to the gasifier, where enough gaseous sulfur dioxide is added to convert the calcium sulfite present to bisulfite and to form some free sulfurous acid. The sulfate then precipitates as $CaSO_4 \cdot 2H_2O$ (gypsum), which, with the ash, is filtered off. Clear effluent from the thickener and filter is alkalized with lime at the liming tank to form a precipitate of calcium sulfite hydrate. The principal reaction at the liming tank is assumed to be:

$$CaO + 2NaHSO_3 + H_2O \rightarrow CaSO_3 \cdot 2H_2O \downarrow + Na_2SO_3.$$

The slurry from the liming tank is returned to the ash clarifier, where the calcium sulfite crystals are collected and pumped with the underflow to the gasifier.

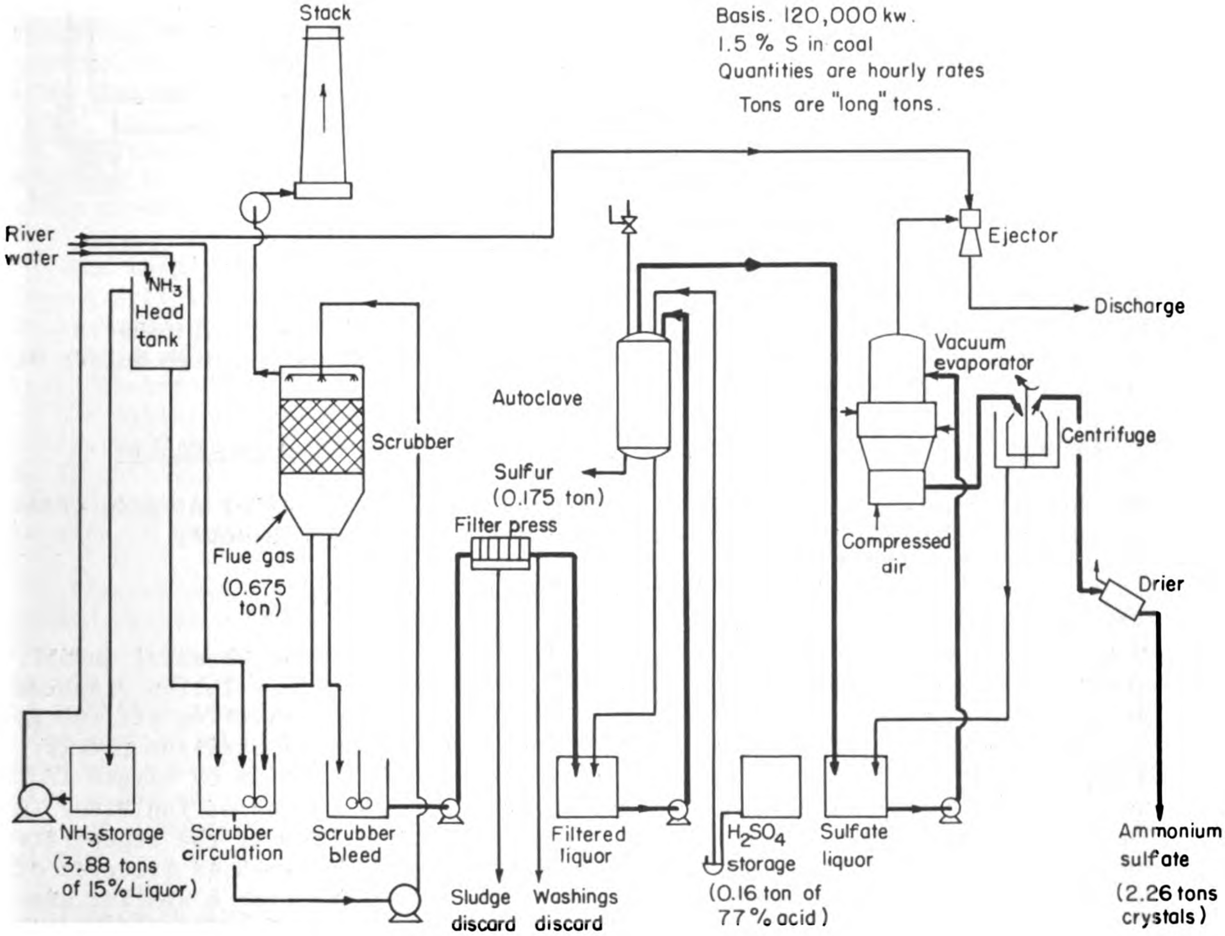


FIGURE 4. - Fulham Simon-Carves Ammoniacal Liquor Process.

(Reproduced From Rees, R. L. (180).)

Original from THE OHIO STATE UNIVERSITY

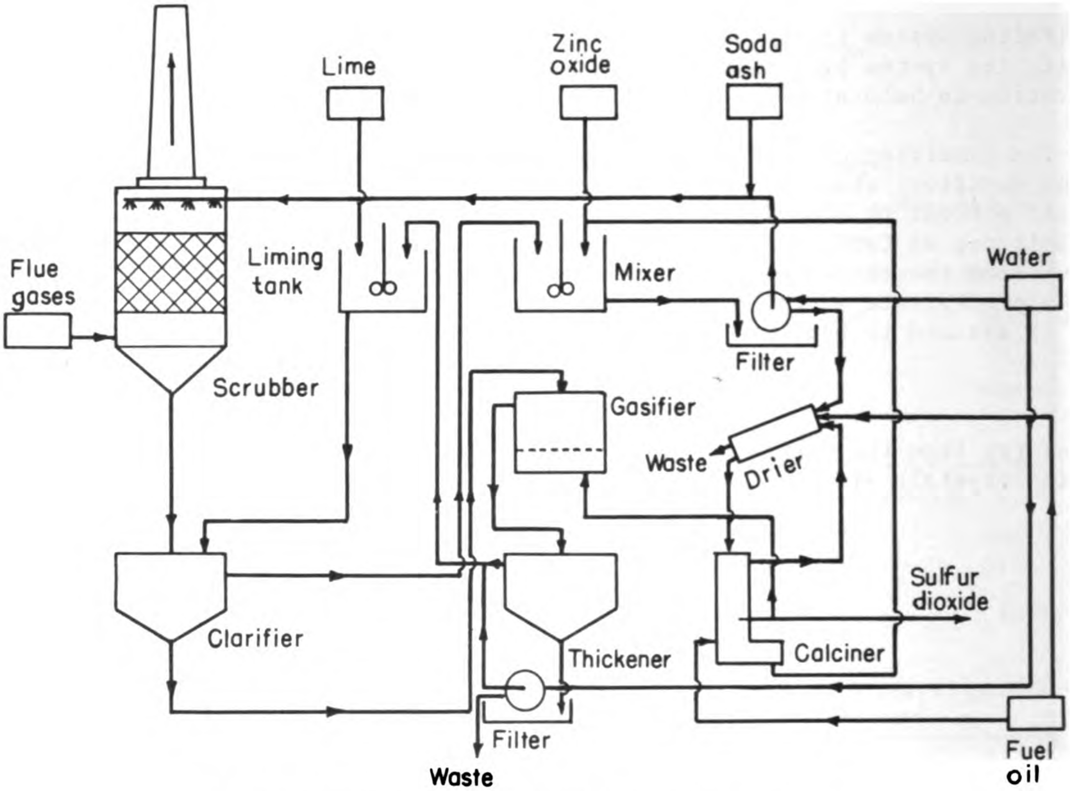


FIGURE 5. - Johnstone and Singh Zinc Oxide Process.
(Reproduced From Rees, R. L. (180).)

If hydrogen chloride is present in the flue gas, soluble zinc chloride is formed. Because of this feature this method is limited to fuels of high sulfur dioxide to chlorine ratio.

Absorption Processes for Gases of High Sulfur Dioxide Concentration

The following cyclic processes were developed to recover sulfur dioxide from more concentrated streams as in the roaster gases from smelting plants.

Basic Aluminum Sulfate Process - I.C.I. (2)

The basic aluminum sulfate process developed by the Imperial Chemical Industries in England employs as absorbent a soluble basic aluminum sulfate solution prepared by treating a solution of aluminum sulfate with limestone and filtering off the gypsum formed. Phosphoric acid is added to inhibit formation of the crystalline precipitate ($Al_2O_3 \cdot SO_3 \cdot 3.5H_2O$). Oxidation of sulfur dioxide to sulfur trioxide by oxygen in the gas can be inhibited by the presence of methylene blue, but losses of inhibitor in the process are considered excessive. In practice a side stream of the regenerated-absorbent solution is treated with limestone, and the gypsum formed is filtered off to control the sulfate content of the solution. When employed with a smelter gas containing 5 percent sulfur dioxide, a tail gas of 0.2 percent or less sulfur dioxide is obtained. This process, however, is unsuitable for gases containing less than 1 percent sulfur dioxide.

The first commercial plant was put into operation in 1936 and operated 5 years at a copper-smelter plant at Imatra, Finland. The only plant now using this process is operated at Manchester, England, at a rate of 7 to 8 tons of liquid sulfur dioxide per day (114).

Use of Amines

The application of still other systems for the cyclic method of sulfur dioxide recovery, involving absorption and subsequent regeneration of the solution, has been proposed. One such system employs a methylamine-water (107) solution, which requires a larger quantity of steam for regenerating the solution than does the ammonia system; but, because of the nonvolatility of the base, regeneration may be carried further than with ammonia solutions; consequently, sulfur dioxide may be removed from the gas more completely with less circulating solution.

Ethanolamine, which is used commercially for recovering hydrogen sulfide and carbon dioxide (17), required about 25 percent less steam than the ammonia solutions. Unfortunately, spontaneous oxidation of the sulfite to sulfate took place rapidly in flue gases and rendered the solution useless (107).

Much work on using other amines as absorbents for sulfur dioxide has been carried out. Those mentioned in the literature include: Diethylenetriamine, triethyltetramine, ethylamine, and diethanolamine (188). Mixtures of pyridine, quinoline, isoquinoline, acridine, aniline, p-toluidine, xylidine, or triethanolamine with one of the following: Lactic acid, citric acid, glycerol, ethylene glycol, diethylene glycol, and resorcinol in contact with water, have been suggested (16). Absorption of combustion gases with mixtures of triethanolamine, ethanolamine and potassium carbonate in the ratio of 2:2:1 has been used. Ninety-five to 98 percent of the acidic gases (CO_2 and SO_2) can be removed(15).

The Lurgi "sulfidine process" (236) developed in Germany makes use of a suspension of xylidine or toluidine in water as absorbent. Xylidine and water are immiscible; however, as sulfur dioxide is absorbed, the xylidine sulfite tends to dissolve. When the dioxide concentration in the solution approaches 100 grams per liter, the absorbent becomes homogeneous. For regeneration steam drives off the sulfur dioxide, and the xylidine and water separate. When this type of scrubbing is used with a gas containing 8 percent sulfur dioxide, a tail gas of 0.05 to 0.10 percent sulfur dioxide is obtained. The system is not economical for gases of low sulfur dioxide concentration owing to loss of xylidine in the waste gases. The Lurgi "sulfidine process" was used in Germany before World War II, and a plant existed in Hamburg in 1946 (155).

Fleming and Fitt (58) used dimethylaniline, which is anhydrous, in place of a xylidine-water mixture. In this process (see fig. 6) the gases are first treated to remove particulate matter and are then passed to an absorbing tower in which they are contacted countercurrently with dimethylaniline, which absorbs the sulfur dioxide. The purified gases are then contacted with a solution of sodium carbonate, which removes some or all of the sulfur dioxide escaping the absorbing tower and also collects any entrained dimethylaniline carried over from the absorbing tower. The waste gases are finally contacted with a dilute sulfuric acid solution, which reacts with any dimethylaniline vapor in the waste gases and absorbs it in the acid as the sulfate.

The rich dimethylaniline solution from the absorber passes through heat exchangers and then to a stripping tower, where the sulfur dioxide is stripped out of the dimethylaniline by contact with steam. The sulfur dioxide driven off from the dimethylaniline is cooled to condense some water and dimethylaniline vapors, which go overhead from the stripping tower. After the cooling step the sulfur dioxide passes to the dehydrating tower and then to its ultimate use.

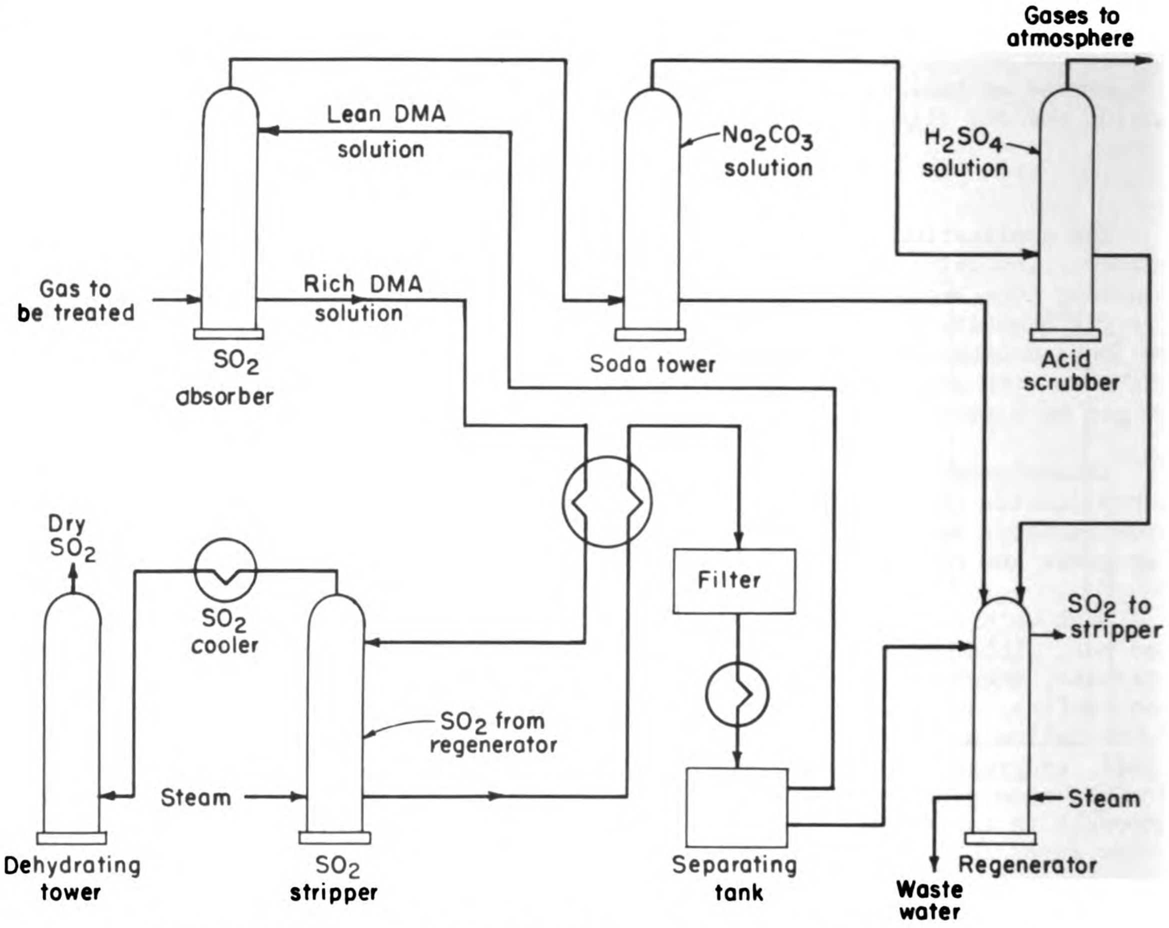


FIGURE 6. - Fleming and Fitt Dimethylaniline Process. *(Reproduced From Magill, P. L., Holden, F. R., and Ackley, C. (135).)*

The lean solution from the stripping tower is passed through heat exchangers and a filter and finally returned to a decanting tank to separate the dimethylaniline from entrained water. The decanted dimethylaniline is then returned to the absorber for further pickup of sulfur dioxide. Effluent solutions from the sodium carbonate tower, the acid towers, and the water-decanting tank are treated in a dimethylaniline regenerator with steam. In this tower the dimethylaniline is distilled from these solutions and returned to the sulfur dioxide stripping tower (135). There are two plants - the Selby, Calif., plant of the American Smelting and Refining Co. and the Copperhill, Tenn., plant of the Tennessee Copper Co. Gas of a purity of >99.99 percent sulfur dioxide is obtained (25).

Urea solutions (107), which are very weak bases, should have high-temperature coefficients, but they have such low capacities for absorbing sulfur dioxide that they cannot be considered.

Magnesium Hydroxide

Another method (133) of absorbing sulfur dioxide is using an aqueous suspension of magnesium hydroxide $[Mg(OH)_2]$. Magnesium sulfite and sulfate are formed and passed to a tank, where the mixture is first aerated and then allowed to settle. The solution of magnesium sulfate is withdrawn from the top of the tank, and ammonia is injected into it to regenerate the magnesium hydroxide. Ammonium sulfate is formed as a byproduct.

A process using magnesium oxide suspended in water was tried on a pilot-plant scale in the U.S.S.R. Sparingly soluble magnesium sulfite was precipitated. It was separated from the scrubbing liquid, dried, and calcined to give sulfur dioxide and magnesium oxide, which was reused. Magnesium sulfite and sulfate accumulated in the circulating solution. A portion of the stream was bled off. The sulfite was oxidized to sulfate and the magnesium sulfate recovered by crystallization (155).

ADSORPTION OF SULFUR DIOXIDE

The mechanism by which surface adsorption takes place is not actually known. It is probably a combination of three separate effects:

(1) The formation on the surface of the solid of a layer of the adsorbed vapor 1 molecule deep.

(2) The formation of a second layer of variable thickness held by the attraction between the solid and the vapor, the thickness depending on the strength of the attraction.

(3) The collection on the surface in submicroscopic capillary openings of a more or less condensed layer of vapor (189, 241).

These three effects are shown in figure 7. The solid will adsorb vapor from A to B when the partial pressure of the vapor in the gas is virtually zero. When point B is reached, an increase in pressure is needed to increase the adsorption; the range B to C is due to molecular attraction and the range from C to D to capillary condensation.

A number of formulas have been developed to express the relationship between the quantity of vapor adsorbed per unit quantity of solid as a function of the partial pressure of the vapor. All apply to equilibrium conditions.

Freundlich Adsorption Equation

$$\frac{x}{m} = a\,p^{1/n} \quad (65);$$

x = weight or volume of vapor adsorbed;
m = weight of solid;
p = partial pressure of vapor;
a, n = experimental constants;
$n > 1$.

If the data fit the empirical Freundlich equation, a plot of $\log \frac{x}{m}$ as a function of $\log p$ should give a straight line of slope $\frac{1}{n}$ and intercept of $\log a$.

Langmuir Equation (126)

This equation is based on the assumption that the adsorbed vapor is 1 molecule deep and the greater the fraction of the surface so covered the less the tendency for more adsorption and the greater the partial pressure necessary for further adsorption.

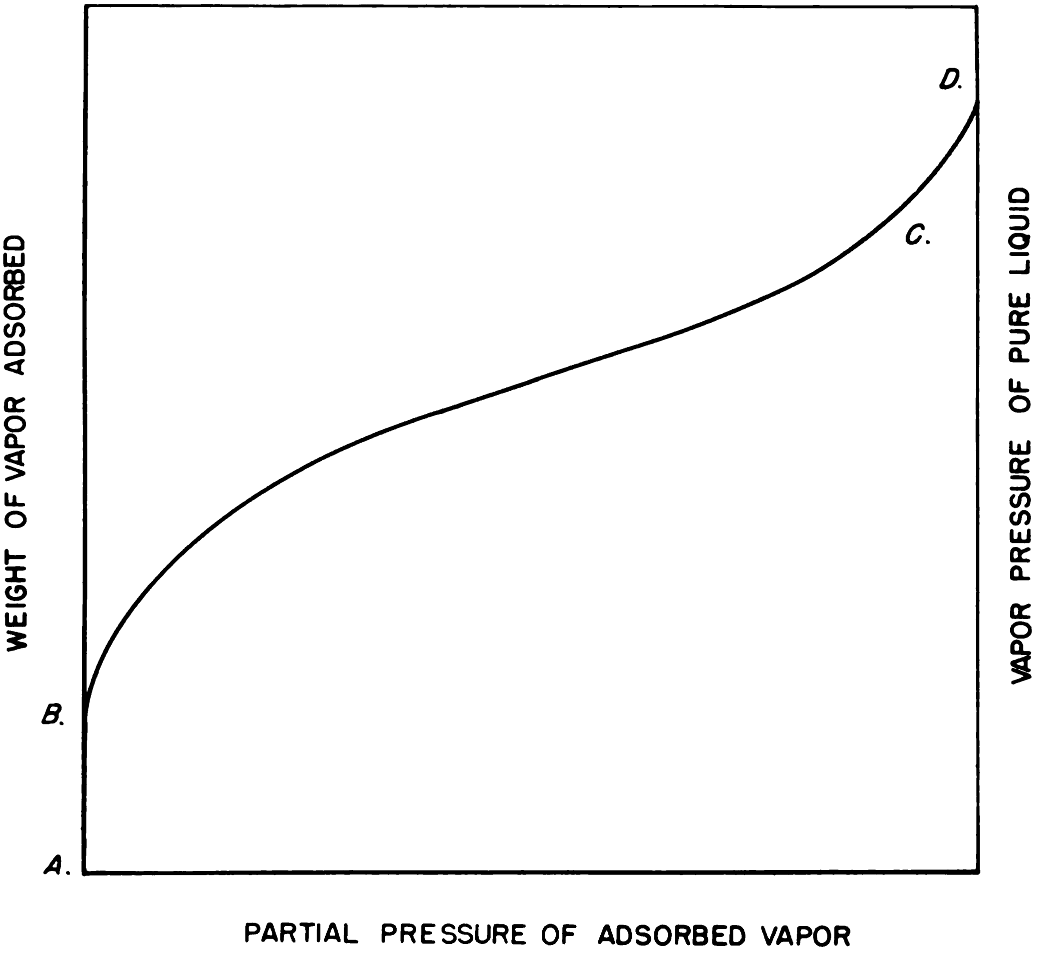


FIGURE 7. - Typical Adsorption Curves for Charcoal.
(Reproduced From Robinson, C. S. (189).)

$$\frac{x}{m} = \frac{abp}{1+ap},$$

x = weight or volume of vapor adsorbed,
m = weight of solid,
p = partial pressure of vapor,
a, b = empirical constants.

If the data fit the Langmuir equation, a plot of $\frac{p}{\frac{x}{m}}$ as a function of p should give a straight line.

Patrick Adsorption Equation

Patrick (145) has found that a modified Freundlich adsorption equation can be made to fit adsorption by silica gel with considerable precision. Silica-gel adsorption depends largely on capillary condensation.

$$V = K \frac{P\sigma}{P_o}^{1/n};$$

where

V = volume of adsorbed vapor per unit weight of adsorbing solid;

P = partial pressure of vapor;
P_o = vapor pressure of the condensed liquid;
σ = surface tension of the condensed liquid;
K, n = constants, independent of the vapor but dependent only on the physical characteristics of the solids.

A plot of $\frac{P\sigma}{P_o}$ against the function log V will give a straight line of slope $\frac{1}{n}$. For the system silica gel-sulfur dioxide, $K = 0.1038$, and $\frac{1}{n} = 0.447$, when V is expressed in cubic centimeters, and σ in dyne per centimeter.

Adsorption of Mixed Vapors

Mixtures of vapors are not adsorbed in the same proportion as they exist in the gaseous phase. At the start, all components are readily adsorbed. As the solid approaches saturation the more volatile vapors adsorbed are displaced by the less volatile, so that, when equilibrium is reached, the adsorbed vapor consists largely of the less volatile constituents.

For the theory of adsorption the reader is referred to Brunauer's (21) work and for the practical aspects of adsorption to that of Mantell (138).

Adsorption on Carbon

A comparison of the adsorption of various gases on activated carbon (Kahlbaum) at 15° C. is shown by the following data (182):

Gas	Formula	Cc./gram at 15° C.
Phosgene	$COCl_2$	440.0
Sulfur dioxide	SO_2	379.7
Methyl chloride	CH_3Cl	277.0
Chlorine	Cl_2	234.6
Ammonia	NH_3	180.9
Hydrogen sulfide	H_2S	98.9
Hydrogen chloride	HCl	72.0
Nitrous oxide	N_2O	54.2
Acetylene	C_2H_2	48.9
Carbon dioxide	CO_2	47.6
Methane	CH_4	16.2
Carbon monoxide	CO	9.3
Oxygen	O_2	8.2
Nitrogen	N_2	8.0
Hydrogen	H_2	4.7

One gram of carbon at 15° C. adsorbes 379.7 cc. of sulfur dioxide at 1 atmosphere pressure. The temperature dependence for sulfur dioxide at atmospheric pressure was as follows:

Temperature .... °C.	6.5	12.0	16.0	18.5	25.5	43.5	56.0	71.0	86.0
Adsorbed vol., cc./gm. carbon..	495	408	375	320	261	185	136	97	76

The pressure dependence at 15° C.:

Pressure, mm. Hg. ..	827.5	759.5	649.5	515.5	404.5	322.5	258.5	194.5	126.5	78.5	47.0
Adsorbed vol., cc./gm. carbon	402.9	379.4	320.8	278.9	235.6	195.4	171.9	140.6	101.5	60.4	21.4

In the adsorption of sulfur dioxide from air mixtures (0.3 to 5 percent sulfur dioxide) at 25°, 50°, and 100° C., activated carbon is superior to aluminum oxide gel. Gelatinous silica has a lower saturation value than aluminum oxide or active carbon, but it is superior in that it is more easily activated and cheaper (53).

Activated carbon that has been iodized has a greater adsorptive power for sulfur dioxide in airstreams. At 20° C. its adsorptive capacity for sulfur dioxide in a concentration of 0.05 percent is 1.8 times as great as pure activated charcoal and 1.2 times as great when the concentration is 0.02 percent (176).

An aqueous suspension of carbon dust (collected from the flue chamber of a coal-burning furnace) is effective in removing sulfur dioxide. When the exit gas containing 0.7 percent sulfur dioxide from a contact acid plant was passed at a rate of 300 liters per minute through 600 liters of carbon dust in 135 cubic meters of water, 94 percent was removed (67).

Adsorption on Silica Gel

In a series of papers Miller (150) considers the basic factors in the adsorption of vapors by silica gel - the effects of temperature, pressure, and the resistance of bed. The adsorption isotherms of sulfur dioxide on silica gel are shown in figure 8.

The maximum adsorption of sulfur dioxide was found to occur with gels containing 7 percent water. The adsorption of sulfur dioxide on silica gel fits precisely the Patrick adsorption equation as shown on p. 14.

The adsorption of sulfur dioxide on metal-impregnated silica gel at temperatures up to 218° C. was investigated (185). A tabulation of the cubic centimeters of sulfur dioxide adsorbed per gram of adsorbent follows:

Temperature, °C.	Platinized gel	Palladized gel	Copperized gel	Pressure, mm.Hg.
0.0	100.9	136.4	143.2	740-750
64.5	30.8	34.7	41.7	740-750
100.0	12.0	20.8	21.2	740-750
138.0	7.3	10.0	11.7	740-750
218.0	1.3	2.6	6.2	740-750

The activated adsorption of sulfur dioxide, oxygen, and mixtures of sulfur dioxide and oxygen by a catalyst composed of silica gel containing 5 percent of vanadium oxide was studied (1). Adsorption of sulfur dioxide took place in the range of 290° to 480° C. At a given temperature and pressure, adsorption of sulfur dioxide was 5 times as much as oxygen.

Adsorption on Platinum

The adsorption isotherms from 20° to 250° C. on platinum black show the customary form, decreasing with increase in temperature and agreeing with the Freundlich

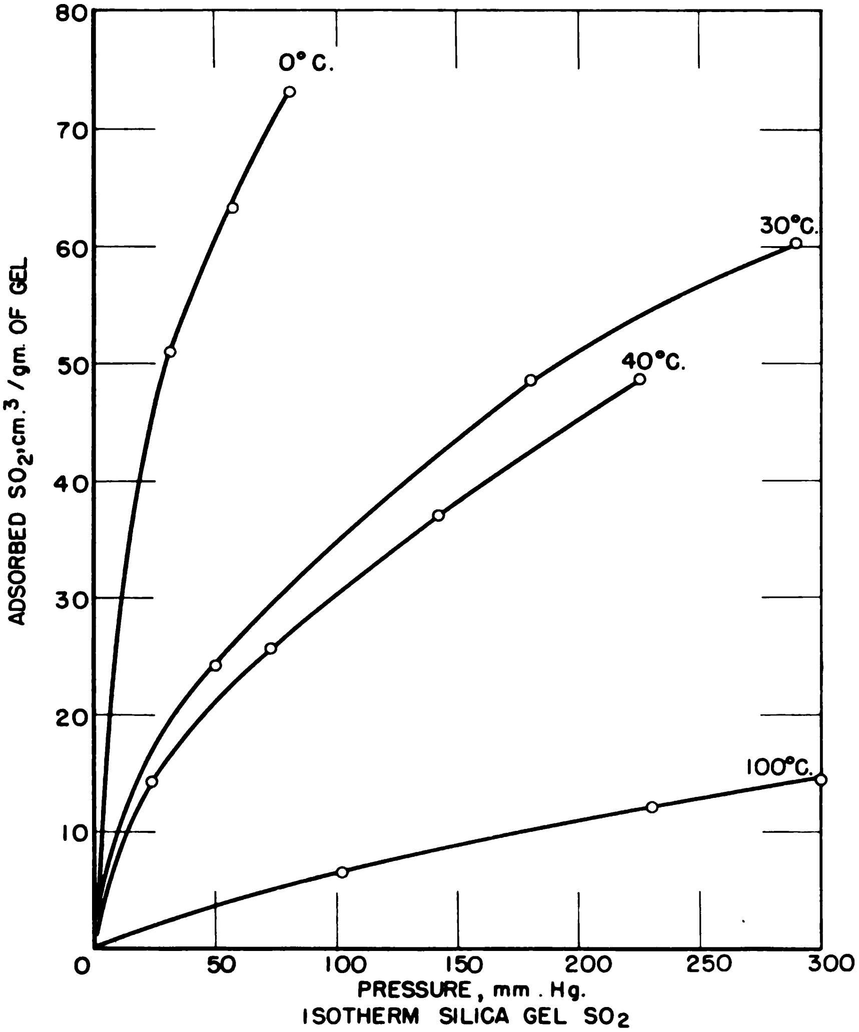


FIGURE 8. - Adsorption of SO_2 in Cm.^{3}/Gm. of Gel at 0°, 30°, and 100° C.
(Reproduced From Miller, E. B. (150).)

equation. The isotherms at 300° and 400° C. due to chemical reaction ($3SO_2 = 2SO_3 + S$) show a completely different course. The isotherms of sulfur dioxide on platinum are shown in figure 9 (159).

The adsorption data in terms of the Freundlich equation, $A = \alpha p^{1/n}$, are:

Temperature, ° C.	$\log_{10}p$	α	1/n
20	0 - 2.1	0.005	1.12
	2.1 - 3.0	.105	.52
50	0 - 2.1	.011	.94
	2.1 - 3.0	.059	.60
100	0 - 2.2	.0004	1.49
	2.2 - 3.0	.011	.83
200	2.1 - 3.0	.0035	.93
250	2.1 - 3.0	.0042	.86

A = cc. sulfur dioxide per gram platinum;
p = partial pressure of gas, mm. Hg.

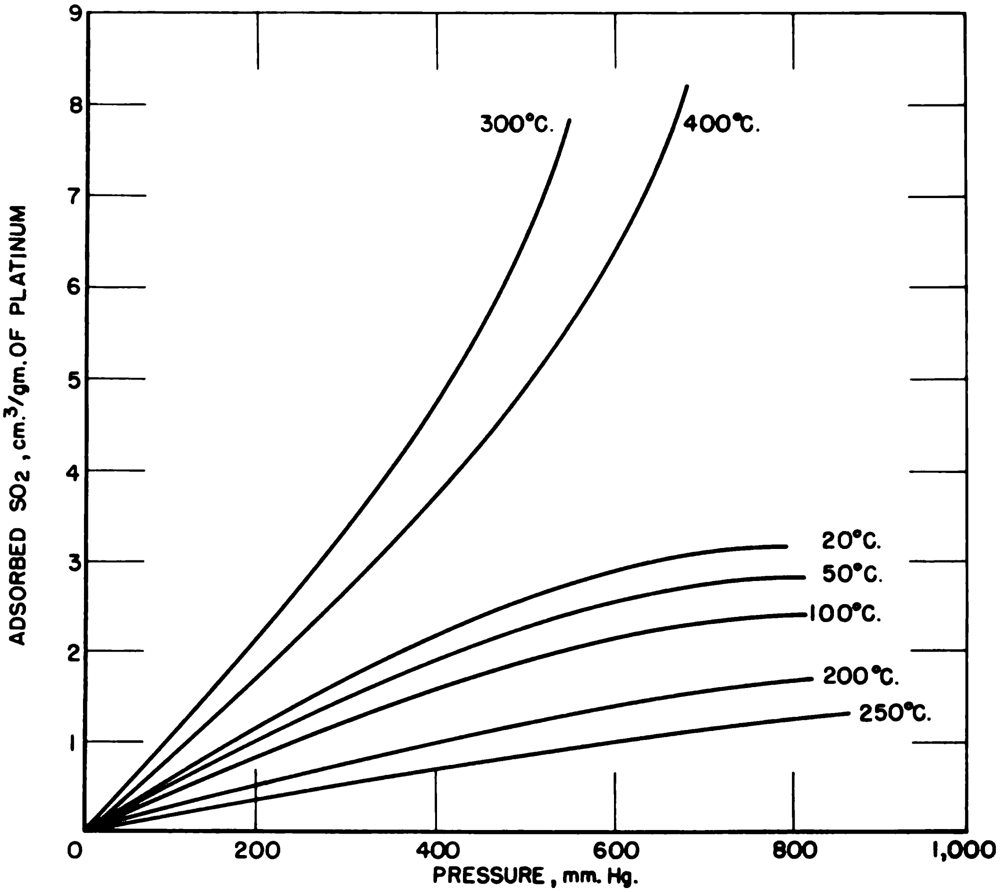


FIGURE 9. - Adsorption Isotherms of Sulfur Dioxide on Platinum Black.
(Reproduced From Neumann, B. and Goebel, E. (159).)

To remove it completely from platinum black, sulfur dioxide must be pumped off for a long time at an elevated temperature. During this process a deterioration of the platinum surface occurs by sintering (159). At room temperature, only about one-fifth of the adsorbed quantity of sulfur dioxide can be removed; at a red glow, complete removal is possible. During this process platinum black is transformed to platinum sponge (154). The irreversible adsorption system of sulfur dioxide and platinum black has been studied more recently (207). With platinized asbestos, the adsorption of sulfur dioxide is reversible, and there is a complete absence of hysteresis (206).

Adsorption on Oxides of Chromium

A very active chromium oxide was prepared by heating $Cr(NO_3)_3 \cdot 9H_2O$ at 250° C. in a stream of hydrogen. Sulfur dioxide adsorption takes place very rapidly, and in comparison with platinum and iron oxide the adsorption of sulfur dioxide is much greater. The isotherms at 20°, 100°, 200°, and 400° C. are reversible and follow Freundlich's equation. Oxidation of sulfur dioxide to sulfur trioxide does not occur (159).

The following data were obtained for the Freundlich equation, $A = \alpha \, p^{1/n}$:

Temperature, °C.	$\log_{10}p$	α	1/n
20	0 - 2.6	0.166	0.61
	2.6 - 3.0	.890	.33
100	0 - 2.4	.118	.64
	2.4 - 3.0	.617	.34
200	0 - 2.5	.091	.66
	2.5 - 3.0	.538	.35
400	0 - 3.0	.105	.55

A = cc. sulfur dioxide per gram adsorbent;
p = partial pressure of the gas, mm. Hg.

When the temperature increases, the adsorption decreases more rapidly than would be expected from the linear relationship between log p and $\frac{1}{T}$. By extrapolation of the data to 575° C., the temperature at which chromium oxide is most active as a catalyst in the contact process, one obtains the following adsorption values, disregarding the sintering of the oxides which occur (159):

Temperature, 575° C.

Pressure .... mm. Hg.	56	110	150	400	830
Adsorbed quantity of sulfur dioxide in cc./gm. Cr_2O_3	0.25	0.5	1.0	2.0	3.0

Adsorption on Oxides of Iron

The adsorption curves at 20° and 100° C. on iron oxide, prepared from iron carbonyl, satisfy Langmuir's equation. Adsorption is of the same order of magnitude as on platinum. At 200° and 400° C. a chemical reaction sets in ($Fe_2O_3 + SO_2 = FeSO_4 + FeO$). The extent of the reaction was the same at both temperatures because of sintering and decrease in area at 400° C., when 75 percent of the sulfur dioxide is chemically bound and 25 percent physically bound (159).

The following data were obtained for the Freundlich equation, $A = \alpha\, p^{1/n}$ (159):

Temperature, °C.	$\log_{10}p$	α	1/n
20	0 - 2.1	0.0055	1.16
	2.1 - 3.0	.240	.40
100	0 - 2.3	.0408	.75
	2.3 - 3.0	.126	.41
200	0 - 3.0	.100	.38

A = cc. sulfur dioxide per gram adsorbent;
p = partial pressure of the gas in mm. Hg.

Perry (172) employed an iron hydroxide gel with a water content of 6.36 percent, prepared from $Fe(NO_3)_3$ and ammonia solution, washed free of nitrate and dried at 100° C. He determined isotherms for sulfur dioxide alone and for sulfur dioxide-air mixtures. The addition of air to the pure gas caused a marked lowering of the saturation capacity of the gel. Saturation value for sulfur dioxide alone was 13.0 grams vapor per 100 grams gel and for the sulfur dioxide-air mixture 10.9 grams vapor per 100 grams gel.

Adsorption on Oxides of Vanadium

The isotherm at 20° C. is normal, showing an adsorption of 0.40 cc. per gram of vanadium pentoxide at 760 millimeters Hg. At 100° C. the saturation is not established, indicating that the reaction $V_2O_5 + SO_2 = V_2O_4 + SO_3$ is taking place. At 500° C. reaction between sulfur dioxide and vanadium pentoxide rather than adsorption is considered to be the mechanism through which oxidation of sulfur dioxide to sulfur trioxide occurs (160).

The adsorption of sulfur dioxide on a catalyst consisting of silica gel with 5 percent vanadium pentoxide was measured between 200° and 500° C. Activated adsorption was found in the range between 290° and 480° C. At a given temperature and pressure, adsorption of sulfur dioxide was more rapid than oxygen, and approximately 5 times as much sulfur dioxide as oxygen was adsorbed (1).

REACTION OF SULFUR DIOXIDE WITH METALS AND METALLIC OXIDES

The reactions of sulfur dioxide with metals and metallic oxides are discussed in this section. If these materials were effective absorbents of sulfur dioxide at flue-gas temperatures, a hot-solid-phase absorption could be employed. The cooling of the gases and the subsequent loss in buoyancy associated with liquid-phase-absorption processes would be avoided.

Reaction with Metals

Copper

Dried air containing 0.01 to 10 percent sulfur dioxide does not affect copper at 25° C. When water vapor is present, corrosion of the copper occurs. Between 63 and 75 percent relative humidity, the rate of attack increases profoundly, pointing to the existence of a critical humidity between these values. The reaction product consists of copper sulfate. When more than 1 percent sulfur dioxide is present, free sulfuric acid is also formed (230). A more recent study (151) on the oxidation of copper at temperatures from 88° to 172° C. shows that sulfur dioxide accelerates the oxidation of bare-copper surfaces. The primary reaction taking place is $6Cu + SO_2 = 2Cu_2O + Cu_2S$. Cuprous sulfate is also formed in a secondary reaction.

The reaction $6Cu + SO_2 = 2Cu_2O + Cu_2S$ is a case of equilibrium in a univariant system, a definite pressure of sulfur dioxide corresponding to each temperature.

Temperature .... °C.	586	607	636	650	669	691	710	730	(181)
SO_2 pressure .... mm. Hg.	73	120	179	222	289	390	488	599	

For higher temperatures:

Temperature .... °C.	726.5	768	810.5	851.5	893	931.5	(217)
SO_2 pressure ..... mm. Hg.	690	1,103	1,649	2,304	3,052	3,770	

This reversible reaction is affected by adding other compounds: (a) Gold, palladium, and platinum added to copper increase the equilibrium pressure; (b) Fe_2O_3, Mn_2O_3, and Cr_2O_3, form compounds of the type $Cu_2X_2O_4$, which decrease the pressure, for example, at 700° C. in presence of Fe_2O_3 the equilibrium pressure of sulfur dioxide drops from 435 mm. to 43 mm. Hg; (c) in the presence of MnS and CoS is a decided decrease in equilibrium pressure (196).

Iron

The attack of dry sulfur dioxide on soft iron becomes noticeable above 200° C. and severe in the range of 800°-1,000° C. The scale formed consists of FeS, Fe_3O_4, and FeO. Carbon in steel reduces the attack (7).

The reaction $3Fe + SO_2 = FeS + 2FeO$ takes place at 300° to 1,000° C. when sulfur dioxide is passed over iron. Only at very high temperatures is the reaction reversible (95). Hatfield (92) also investigated the attack of sulfur dioxide on iron to 1,000° C.

Magnesium

The reaction between magnesium and sulfur dioxide begins at about 400° C. It proceeds heterogeneously between 500° and 800° C. probably according to the following reactions (200):

$$3\ Mg + SO_2 \rightarrow 2MgO + MgS + 300.1\ kcal., \qquad (1)$$
$$MgS + 2\ SO_2 \rightarrow MgSO_4 + S_2 + 81.1\ kcal., \qquad (2)$$
$$MgSO_4 \rightarrow MgO + SO_2 + 1/2\ O_2 - 85.6\ kcal., \qquad (3)$$
$$Mg + 1/2\ O_2 \rightarrow MgO + 145.8\ kcal., \qquad (4)$$
$$(1) + (2)\ 3\ Mg + 3\ SO_2 \rightarrow 2\ MgO + MgSO_4 + S_2 + 381.2\ kcal., \qquad (5)$$
$$\text{Overall}\ 4\ Mg + 2\ SO_2 \rightarrow 4\ MgO + S_2 + 441.4\ kcal. \qquad (6)$$

At 600° C. reaction (5) was verified by experiment. At 700° C. reaction (6) was found to take place (199). At 700° C. the dissociation of $MgSO_4$ according to (3) is appreciable. The intermediate reactions giving equation (3) are as follows:

$$MgSO_4 \rightleftharpoons MgO + SO_3, \qquad (7)$$
$$2\ SO_3 \rightleftharpoons 2\ SO_2 + O_2, \qquad (8)$$
$$[2 \times (7)] + (8)\ 2\ MgSO_4 \rightleftharpoons 2\ MgO + 2\ SO_2 + O_2.$$

The temperature of 700° C. is not enough for the complete reduction of sulfur dioxide by means of magnesium. The reaction is heterogeneous and is confined to the interface of the components. The reaction products are insoluble in magnesium and form a protective coat. The rate of the reaction corresponds with rates calculated from Fick's diffusion laws. Above 650° C. the reaction velocity is proportional to the vapor pressure of magnesium. At around 1,100° C. the protective coating is destroyed mechanically owing to the boiling of the magnesium, and ignition takes place. This ignition temperature is so reproducible that the boiling point of magnesium, 1,106° C., can be determined this way (199).

Nickel

At 350° C., pyrophoric nickel reacts with sulfur dioxide and forms a NiO-NiS mixture. When hydrogen is present the oxide is reduced and the sulfur content is diminished toward that required by formation of the subsulfide (Ni_3S_2) (88).

At 550° C. nickel powder reacts with sulfur dioxide at atmospheric pressure quantitatively according to the reversible reaction (197):

$$3\ Ni + SO_2 = 2\ NiO + NiS \qquad -61{,}700\ cal.$$

At 800° C., sulfur dioxide attack is very heavy but decreases with higher temperatures owing to the formation of a strongly adherent protective coating. At 1,000° C. the attack is negligible (92).

Original from THE OHIO STATE UNIVERSITY

Reaction With Metallic Oxides

Aluminum Oxide

Aluminum oxide (or silica) in mixture with calcium oxide is strongly acted on by sulfur dioxide at about 400° C., but with aluminum oxide or silica alone the reaction does not occur (93).

Aluminum hydroxide dried at 100° C. absorbs sulfur dioxide at room temperature from mixtures of SO_2-O_2 without oxidation of the sulfur dioxide (192).

Calcium Oxide

At room temperature sulfur dioxide does not react with dry calcium oxide, although it does react with $Ca(OH)_2$. At 350° C. almost complete conversion to the sulfite is obtained. This sulfite decomposes at higher temperatures to sulfide and sulfate.

At 400° C. Veley found that sulfur was formed abundantly (229) perhaps because of the presence of water vapor in the gas. When dry sulfur dioxide is used only traces of sulfur are formed (91).

When sulfur dioxide is passed over CaO, CaO + ZnO, or CaO + PbO, at 650° to 700° C., sulfide and sulfate are formed. At 950° C. sulfur dioxide reacts with calcium oxide in the proportion of 1:1 almost quantitatively; at 1,100° C. only partly, probably owing to the reversible reaction (227):

$$4\ CaO + 4\ SO_2 \rightleftarrows CaS + 3\ CaSO_4.$$

At 1,150° C. there is still some reaction; at 1,200° C. reaction ceases (29).

For reactions and equilibrium pressures in the system CaO, CaS, $CaSO_4$, SO_2 between 900° and 1,200° C., see Zawadzki, and others (251).

Oxides of Copper

Cuprous Oxide

Sulfur dioxide does not react with cuprous oxide at moderate temperatures nor at a red heat.

The reaction, $6\ Cu + SO_2 \rightleftarrows Cu_2S + 2\ Cu_2O$, is discussed on p. 20.

Cupric Oxide

Sulfur dioxide reduces cupric oxide at 450° C. quantitatively (116).

$$3\ CuO + SO_2 = CuSO_4 + Cu_2O.$$

When cupric oxide is heated with a mixture of sulfur dioxide and oxygen or sulfur dioxide and air, sulfur trioxide is formed. When mixtures of cupric and chromic oxides are used, better yields are obtained (242). Use of cupric oxide alone as a contact catalyst is no longer warranted. The maximum conversion of sulfur dioxide to sulfur trioxide with CuO is 58.7 percent at 700° C.; with $2CuO \cdot Cr_2O_3$ the conversion is 83 percent at 575° C.; with $CuO \cdot Cr_2O_3$ it is 77.5 percent at 600° C. (158).

The free energies of copper and its oxides, sulfides, and sulfites have been tabulated (177).

Oxides of Chromium

Cr_2O_3 remains unchanged with sulfur dioxide at room temperature. When heated in sulfur dioxide gas in the presence of oxygen or air sulfur trioxide is catalytically formed at 400° C. (157, 242).

At room temperature CrO_3 absorbs sulfur dioxide from sulfur dioxide-oxygen mixtures without reaction of the sulfur dioxide with the oxygen (192).

Hydrated CrO_2 and chromium hydroxide dried at 100° C. absorb sulfur dioxide at room temperature from sulfur dioxide-oxygen mixtures; partial oxidation of the sulfur dioxide results.

Oxides of Iron

Sulfur dioxide reacts with Fe_2O_3 slowly at temperatures between 500° and 800° C. to give sulfur trioxide and Fe_3O_4 (116).

$$3\ Fe_2O_3 + SO_2 = 2\ Fe_3O_4 + SO_3.$$

FeO on being heated with SO_2 reacts with incandescence, and clouds of sulfur and sulfur trioxide are evolved. Aqueous extraction of the product yields a residue containing sulfide and Fe_2O_3 and an extract containing Fe^{+2}, Fe^{+3}, and $SO_4^{=}$ ions (91)

Oxides of Lead

PbO, Lead Oxide

Sulfur dioxide reacts with heated lead oxide to form lead sulfide and sulfate. Only slight traces of sulfur and sulfur trioxide are formed (91).

The hypothesized reactions are:

$$4PbO + 4SO_2 \rightarrow PbS + 3PbSO_4,$$
$$PbSO_4 + 10SO_2 \rightarrow PbS + 8SO_3 + 2S.$$

PbO_2, Lead Dioxide

Sulfur dioxide reacts with lead dioxide at room temperature to form lead sulfate (192).

$$PbO_2 + SO_2 \rightarrow PbSO_4.$$

As lead dioxide reacts with sulfur dioxide directly and appears to be uninfluenced by the presence of water, it can be used as a means of measuring low concentrations of sulfur dioxide in the atmosphere. A water-mixed paste of PbO_2, dried and supported on a cotton cloth, was quite effective for quantitative measurements. There was very little diminution in the rate of absorption up to a conversion of 30 percent of the reagent (240).

Oxides of Manganese

MnO, Manganous Oxide

When sulfur dioxide is passed over heated MnO, sulfur and sulfur trioxide are given off, and the residue is a green powder containing MnS, $MnSO_4$ and traces of higher oxides (Mn_3O_4); when heated longer to a red glow, the residue becomes ultimately white with complete transformation into $MnSO_4$ (91).

The reactions are:

$$7MnO + 10SO_2 \rightarrow MnS + 6MnSO_4 + SO_3 + 2\ S \text{ (primary reaction)},$$
$$MnS + 5MnSO_4 \rightarrow 2Mn_3O_4 + 6\ SO_2,$$
$$Mn_3O_4 + SO_2 \rightarrow 2MnO + MnSO_4.$$

Mn_2O_3, Manganic Oxide

Mn_2O_3 absorbs sulfur dioxide actively at 700° C. according to

$$2Mn_2O_3 + SO_2 \rightarrow Mn_3O_4 + MnSO_4 \text{ (196)}.$$

MnO_2, Manganese Dioxide

In the completely dry state MnO_2 and sulfur dioxide do not react even upon heating. When moist, however, rapid reaction, the formation of $MnSO_4$, and change in color result. Feigl (51) discusses the part played by the water in this reaction and in the H_2S-SO_2 reaction.

In the presence of dried air at room temperature neither absorption of sulfur dioxide nor formation of sulfur trioxide occurs; however, if moisture is also present, both occur (192).

When finely divided MnO_2 is heated to dull redness, interaction with sulfur dioxide takes place with evolution of heat and light; a red-brown powder, containing $MnSO_4$ and one or both of the oxides Mn_2O_3 and Mn_3O_4, remains. Sulfur trioxide and traces of sulfur are also formed. The possible reactions taking place are (91):

$$MnO_2 + SO_2 = MnSO_4,$$
$$2MnO_2 + SO_2 = SO_3 + Mn_2O_3,$$
$$3Mn_2O_3 + SO_2 = 2Mn_3O_4 + SO_3,$$
$$Mn_3O_4 + SO_2 = 2MnO + MnSO_4,$$
$$Mn_2O_3 + MnO = Mn_3O_4,$$
$$MnO + 2MnO_2 + SO_2 = Mn_3O_4 + SO_3.$$

Dithionates are prepared by bubbling sulfur dioxide through a cold aqueous suspension of MnO_2, boiling off the excess sulfur dioxide, filtering off the MnO_2, and then treating the solution with a hydroxide. Crystalline barium dithionate is obtained as follows (190):

$$MnO_2 + 2SO_2 \rightarrow MnS_2O_6,$$
$$MnS_2O_6 + Ba(OH)_2 + 2H_2O \rightarrow BaS_2O_6 \cdot 2H_2O + Mn(OH)_2.$$

MnO_2 when heated with sulfurous acid will give manganic sulfite and nascent oxygen (142).

$$2MnO_2 + 3H_2SO_3 \rightarrow Mn_2(SO_3)_3 + 3H_2O + 1/2\ O_2,$$
$$Mn_2(SO_3)_3 \rightarrow MnS_2O_6 + MnSO_3.$$

Manganese dioxide decomposes to manganic oxide when heated in air to 530° C. and to mangano manganic oxide at about 950° C. (147).

$$4MnO_2 \xrightarrow{530^\circ\ C.} 2Mn_2O_3 + O_2,$$
$$6Mn_2O_3 \xrightarrow{940^\circ\ C.} 4Mn_3O_4 + O_2.$$

Mn_3O_4, Mangano Manganic Oxide

Mn_3O_4 is prepared by ignition of $MnSO_4$ at 1,100° C. (149).

$$3MnSO_4 \xrightarrow{1{,}100^\circ\ C.} Mn_3O_4 + 3SO_2 + O_2.$$

Manganous oxide is formed when Mn_3O_4 is ignited in a stream of hydrogen (149).

$$Mn_3O_4 + H_2 \rightarrow 3MnO + H_2O.$$

Thermochemistry of the oxides: The specific heats, heats of formation, and free energy of formation of the oxides of manganese are reported by Millar (149). The thermochemistry of the oxides of manganese is reported by Simon and Fehér (209).

$$Mn_2O_7 \xrightarrow{0^\circ-23^\circ\ C.} MnO_2 \xrightarrow{307^\circ-600^\circ\ C.} Mn_2O_3 \xrightarrow{800^\circ-1{,}200^\circ\ C.} Mn_3O_4.$$

$$2Mn + 3.5O_2 \rightarrow Mn_2O_7 + 170\ kcal.$$
$$Mn_2O_7 \rightarrow 2MnO_2 + 1.5O_2 + 82\ kcal.$$
$$4MnO_2 \rightarrow 2Mn_2O_3 + O_2 - 26\ kcal.$$
$$4Mn_3O_4 + O_2 \rightarrow 6Mn_2O_3 + 54\ kcal.$$
$$6MnO + O_2 \rightarrow 2Mn_3O_4 + 72\ kcal.$$

The preparation and physical properties of the oxides of manganese, MnO, $Mn(OH)_2$, Mn_3O_4, $\alpha\ Mn_2O_3$, $\gamma\ Mn_2O_3$, $MnOOH$, and MnO_2 have recently been reported (156).

Industrial Applications

Sulfur dioxide has been used industrially in recovering manganese from low-grade ores. An aqueous slurry of the ore is treated with a gas containing nitrogen, oxygen, and sulfur dioxide obtained from burning sulfur in air or roasting sulfide ores.

Manganese Ore Co. Process (228)

1. Sulfur dioxide is passed through a slurry of a low-grade MnO_2 ore to convert the oxide to a soluble sulfate, which is then removed from the gangue.

$$MnO_2 + SO_2 = MnSO_4.$$

Dithionates, thiosulfates, and sulfites are formed in undesirable side reactions:

$$MnO_2 + 2H_2SO_3 = MnS_2O_6 + 2H_2O,$$
$$S + H_2SO_3 = H_2S_2O_3,$$
$$Mn^{++} + H_2SO_3 = MnSO_3 + 2H^+.$$

A low pH inhibits these reactions.

2. The manganese sulfate is thermally dissociated in a rotary kiln:

$$3MnSO_4 \xrightarrow{1,100°-1,200° \text{ C.}} Mn_3O_4 + 3SO_2 + O_2.$$

A variation of this method for removing sulfur dioxide from flue gas has been investigated by the Tennessee Valley Authority (219). A water slurry of oxides of manganese was used to absorb sulfur dioxide from flue gas. The oxides of manganese were obtained by calcining $MnSO_4$ at 1,000° to 1,100° C. At the end of 72 hours the solution contained 29 percent $MnSO_4$; about 10.5 percent of the absorbed sulfur was in the form of dithionate. Only a trace of sulfuric acid was present. The fly ash had not been removed from the flue gas, and it accumulated in the slurry.

Bureau of Mines Proposed Dithionate Process (179)

The manganese dioxide ore is suspended in a strong solution of calcium dithionate, and sulfur dioxide is passed through the slurry. The calcium is precipitated as calcium sulfate, and the manganese goes into solution as manganese dithionate. The solution is treated with milk of lime to precipitate the manganese as the hydroxide and to regenerate the calcium dithionate.

$$MnO_2 + SO_2 \rightarrow MnSO_4,$$
$$MnSO_4 + CaS_2O_6 \rightarrow MnS_2O_6 + CaSO_4\downarrow,$$
$$MnS_2O_6 + Ca(OH)_2 \rightarrow CaS_2O_6 + Mn(OH)_2\downarrow.$$

Oxides of Tin

Dry stannic oxide, SnO_2, is unattacked by sulfur dioxide at a red heat (91).

Stannous oxide reacts with incandescence; it forms clouds of sulfur and only traces of sulfur trioxide.

The primary reaction is a reduction of the sulfur dioxide.

$$18SnO + 7SO_2 = 16SnO_2 + 2SnS + 5S, \quad (1)$$

followed by

$$SnS + 3SnO_2 = 4SnO + SO_2. \quad (2)$$

The SnO formed reacts as in equation (1) until only SnO_2 is present (91).

At room temperature moist SnO_2 absorbs sulfur dioxide from sulfur dioxide-oxygen mixtures without oxidizing the sulfur dioxide (192).

REDUCTION OF SULFUR DIOXIDE WITH GASES

Reduction of sulfur dioxide with gaseous reductants has been extensively investigated, and a number of processes have been commercially adopted. Gas-phase reactions can be carried out readily in industrial equipment, and thus emphasis has been placed on these operations in removing sulfur dioxide.

Reaction With Hydrogen

In the absence of catalysts a dry mixture of sulfur dioxide and hydrogen does not react at temperatures as high as 500° C. (224). At a red heat some sulfur, water, and hydrogen sulfide are formed (11).

Nickel or nickel sulfide (the latter formed during the reaction) acts as a catalyst. The whole of the sulfur dioxide is decomposed at 400° to 450° C. if the gas flow is small. Steam, hydrogen sulfide, and sulfur are formed (224).

Gel catalysts consisting of ferric and aluminum oxides (1:3) and pretreated with hydrogen sulfide to convert the iron oxide to sulfide are particularly valuable for reducing sulfur dioxide with hydrogen. These catalysts may be used as low as 325° C. at atmospheric pressure with hourly space velocities of over 600. At temperatures above 325° C. less active catalysts than the iron-alumina-gel type can be used, such as iron sulfide on various aluminas. Bauxites of high iron content are quite effective after the latter are converted to the sulfide (43).

It was found impossible to reduce sulfur dioxide with hydrogen directly to sulfur without simultaneous formation of hydrogen sulfide. When sulfur dioxide is reacted with enough hydrogen, a mixture of sulfur dioxide, hydrogen sulfide, and sulfur is formed:

$$2SO_2 + 4H_2 = S_2 + 4H_2O,$$
$$2H_2 + S_2 = 2H_2S.$$

Furthermore, when wet gases are reduced the interaction of sulfur with the water vapor originally present plus that produced in the reduction causes the formation of hydrogen sulfide and sulfur dioxide:

$$3/2S_2 + 2H_2O = 2H_2S + SO_2.$$

Doumani (43) suggested a 2-stage process to convert sulfur dioxide to sulfur. In the first stage the gas containing sulfur dioxide was mixed with hydrogen and passed through a catalyst bed (a gel containing about 25 percent iron sulfide and 75 percent alumina) at temperatures above 300° C. In the second stage complete conversion to free sulfur was obtained by introducing into the previously formed hydrogen sulfide more sulfur dioxide and passing the mixed gas over activated alumina at 100°-200° C. The sulfur formed tended to deposit on the catalyst, but the catalyst could be reactivated readily by raising the temperature of the bed to over 500° C.

Equilibrium constants for the reactions with hydrogen:

$$2SO_2 + 4H_2 = 4H_2O + S_2(g); \qquad K_1 = (H_2O)^4\ (S_2)\ /\ (SO_2)^2\ (H_2)^4;$$
$$H_2 + 1/2S_2(g) = H_2S; \qquad K_2 = (H_2S)\ /\ (H_2)\ (S_2)^{1/2};$$
$$SO_2 + 3H_2 = 2H_2O + H_2S; \qquad K_3 = (H_2O)^2\ (H_2S)\ /\ (SO_2)\ (H_2)^3.$$

Temperature .... °C.	300	500	700	900	1,100
log K_1 (130)	22.20	15.64	11.70	9.02	7.06

Temperature ... °K.	298.1	400	600	800	1,000	1,200	1,400
log K_2 (253)	4.79×10^{12}	8.34×10^{8}	1.55×10^{5}	1.95×10^{3}	1.37×10^{2}	23.0	6.38

Temperature .... °K.	1,160	1,362	1,473	1,645
log K_3 (85)	5.58	4.06	3.40	2.54

The equilibrium constants for the reaction of hydrogen sulfide with sulfur dioxide are shown on p. 29.

Reaction With Hydrogen Sulfide

Dry sulfur dioxide and hydrogen sulfide do not react at room temperature and only very slowly at temperatures as high as 300° to 400° C.

Under the influence of a silent electric discharge the gases react very quickly with the separation of sulfur and formation of water (132).

The action of various catalysts is as follows:

Quartz: Fine quartz has good catalyst activity; activated silicic acid is unsuitable as it adsorbs sulfur. Above 400° C. the equilibrium in the presence of quartz sets in quickly; above 500° C., even without a catalyst (90).

Glass and porcelain: The reaction takes place above 300° C. almost entirely on the surface of the vessel or on the porcelain (90) or glass packing (3).

Carbon: Charcoal is activated with steam. The catalyst activity increases with increase in steam temperature. When charcoal is activated at 1,000° C., good activity occurs even at room temperature (247).

Alumina: Doumani and others (43) tried many catalysts for the reduction of sulfur dioxide with hydrogen sulfide. Those catalysts containing aluminum oxide were superior to all others and were effective even with wet gases. Bauxite and precipitated alumina were used at 100° to 200° C., but these catalysts were not as good as highly purified and specially treated alumina such as Alorco, grade A. However, for all catalysts tested complete conversion was obtained below 210° C. at atmospheric pressure. The sulfur tended to deposit on the catalyst and eventually deactivated it. Reactivation was accomplished by raising the temperature of the catalyst above 500° C. See also Doumani's 2-stage process (p. 27).

Smalley and Klohr (211) report the use of the H_2S-SO_2 reaction over a bauxite catalyst to purify sour hydrocarbon gases. They stressed the importance of feeding sulfur dioxide in stoichiometric proportion to the hydrogen sulfide in the gas to get high conversion and stated that 2 stages are required to get 96-percent conversion.

Lee (129) reports on a plant of the Texas Gulf Sulfur Co. for converting sour gases to sulfur. One-third of the gas is burned, and its hydrogen sulfide is converted to sulfur dioxide. The products of combustion are cooled and mixed with the remaining two-thirds of the original gas. The gases enter a catalyst chamber at 230° C. (catalyst composition not given). Here the hydrogen sulfide reacts with the sulfur dioxide to form water and sulfur:

$$2SO_2 + 4H_2S = 4H_2O + 3S_2.$$

A review of similar commercial processes based on the Claus process, developed in Germany about 100 years ago, for recovering sulfur from hydrogen sulfide is given by Gamson and Elkins (68), and also by Graff (86).

Equilibrium constants:

The reaction between sulfur dioxide and hydrogen sulfide takes place as follows:

$$2SO_2 + 4H_2S = 4H_2O + 3S_2; \qquad K_1 = (H_2O)^4\ (S_2)^3\ /\ (SO_2)^2\ (H_2S)^4.$$

At lower temperatures the sulfur vapor polymerizes

$$3S_2 \rightleftarrows S_6, \qquad 4S_6 \rightleftarrows 3S_8.$$

Therefore, for determining the equilibrium the following equations are also to be considered:

$$2SO_2 + 4H_2S = 4H_2O + S_6; \qquad K_2 = (H_2O)^4\ (S_6)\ /\ (SO_2)^2\ (H_2S)^4;$$

$$2SO_2 + 4H_2S = 4H_2O + 3/4S_8; \quad K_3 = (H_2O)^4\ (S_8)^{3/4}\ /\ (SO_2)^2\ (H_2S)^4.$$

Temperature .... °C. (90)	450	500	550	600	650	750	800
K_1	0.85	3.1	9.8	35.5	72.5	129	162

Temperature ..°C. (43)	150	200	250	300	350	400	450	500
K_2	$3x10^{15}$	$5.3x10^{12}$	$4.0x10^{10}$	$9.0x10^{8}$	$3.4x10^{7}$	$2.2x10^{6}$	$2.3x10^{5}$	$3.2x10^{4}$
K_3	$1.2x10^{17}$	$2.5x10^{15}$	$1.4x10^{11}$	$3.3x10^{9}$	$6.9x10^{7}$	$2.9x10^{6}$	5/ $1.8x10^{7}$	$2.0x10^{4}$

Reaction With Carbon Monoxide

The reaction, $2SO_2 + 4CO = 4CO_2 + S_2$, in the absence of a catalyst, proceeds very slowly, even at temperatures as high as 800° C., but almost any hot surface is capable of catalyzing the reaction at this temperature (131).

At 500° C. with bauxite a 97 to 99 percent conversion is achieved (248). Lepsoe (131) states that alumina in the slightly hydrated and acid form is an efficient catalyst at temperatures of 250° to 500° C. Other suitable catalysts are pumice stone that has been impregnated with iron sulfate solution or with Mohr's salt and ignited at 1,000° C., FeS and CaS (246), BaS, Chamotte, pumice stone impregnated with $CaSO_4$ or $BaSO_4$. Visconti (216) used compounds containing vanadium oxides with a zeolite base or other base-exchange compounds at 600° C.

In the Bolidens Gruvaktiebolag (Sweden) process (2) a reducing gas mixture, predominantly carbon monoxide, converts the sulfur dioxide from a copper smelter gas containing 5 percent sulfur dioxide. In the Trail process (131) reduction of sulfur dioxide by carbon monoxide was used for final cleanup following a coke reduction of smelter gas.

5/ This may be a misprint in the original reference.

Bolidens Process (2)

Manufacture of Reducing Gas.

The reducing gas is prepared by a process similar to manufacturing producer gas. A portion of the gas containing sulfur dioxide is diluted with air and then blown by fans through red-hot coke. The principal reactions are:

$$C + O_2 = CO_2 + 97 \text{ kcal.,} \qquad (1)$$
$$CO_2 + C = 2CO - 37 \text{ kcal.,} \qquad (2)$$
$$SO_2 + C = CO_2 + 1/2S_2 + 13 \text{ kcal.,} \qquad (3)$$
$$SO_2 + 2C = 2CO + 1/2S_2 - 24 \text{ kcal.} \qquad (4)$$

Other substances that are formed are COS, CS_2, and H_2S.

Catalytic Reduction of Sulfur Dioxide by the Reducing Gas

The remainder of the raw gas is then added and passed over a catalyst. The following principal reaction occurs:

$$SO_2 + 2CO = 2CO + 1/2S_2 + 50 \text{ kcal.} \qquad (5)$$

Other reactions taking place simultaneously are:

$$SO_2 + 2COS = 2CO_2 + 3/2S_2 + 10 \text{ kcal.,} \qquad (6)$$
$$SO_2 + 2H_2S = 2H_2O + 3/2S_2 - 8 \text{ kcal.,} \qquad (7)$$
$$SO_2 + CS_2 = CO_2 + 3/2S_2 + 0 \text{ kcal.} \qquad (8)$$

Cooling of Gases and Separation of Condensed Sulfur by Electrostatic Precipitation

The Bolidens process was operated for several years in Sweden, but was discontinued in 1943 because of increasing coke prices during the World War (114).

Trail Process

The carbon monoxide and carbonyl sulfide reactions shown on this page (equations 5 and 6) come into use as a step subsequent to a preliminary reduction of the sulfur dioxide in smelter gas by hot carbon. The exit gas from the reduction furnace is cooled to about 500° C. and is passed on to catalyst chambers; the appropriate quantity of fresh sulfur dioxide to bring the ratio of SO_2 : (CO+COS) to 1 : 2 is added. During the cooling of the gas from the reduction furnace the conversion of CO to COS proceeds rapidly. To maintain the efficiency of the alumina catalysts the gas must be freed from dust by purification through electrostatic or other means. The final step in the process consists of condensing sulfur vapor and separating the mist, which is accomplished by known means. The transformation and condensation is given as S_2 (gas) $\rightarrow S_6 \rightarrow S_8 \rightarrow$ S (liquid).

Thermodynamics:

(1) $2SO_2 + 4CO = 4CO_2 + S_2$; $K_1 = (CO_2)^4 (S_2) / (SO_2)^2 (CO)^4$;

(2) $2CO + S_2 = 2COS$; $K_2 = (COS)^2 / (CO)^2 (S_2)$;

(3) $2COS = CO_2 + CS_2$; $K_3 = (CO_2) (CS_2) / (COS)^2$;

(4) $2COS + SO_2 = 2CO_2 + 3/2S_2$; $K_4 = (CO_2)^2 (S_2)^{3/2} / (COS)^2 (SO_2)$.

Temperature ...°C. (246)	700	800	900	1,000	1,100	1,200	1,300
K_1	2.9×10^{14}	1.6×10^{12}	2.5×10^{10}	5.3×10^{8}	2.33×10^{7}	1.54×10^{6}	1.41×10^{5}

Temperature ...°C. (208)	600	700	800	900	1,000	1,100	1,200
K_2	1,270	88	10	1.71	0.38	0.105	0.035

Temperature ...°C. (118)	300	400	480	950
K_3	0.068	0.086	0.154	0.246

Temperature ...°C.	600	700	800	900	1,000	1,100	1,200
K_4[6/]..........	5.17×10^{3}	4.25×10^{3}	3.60×10^{3}	3.16×10^{3}	2.82×10^{3}	2.56×10^{3}	2.36×10^{3}

Standard free energy change (208), calories:

Reaction 1. $\Delta F.^\circ = -99{,}010 + 0.170\ T \log T - 2.12\times10^{-3}\ T^2 + \frac{1.86\times10^5}{T} + 52.14\ T.,$

Reaction 2. $\Delta F.^\circ = -49{,}700 - 11.12\ T \log T + 0.810\times10^{-3}\ T^2 + \frac{3.600\times10^5}{T} + 74.26\ T.,$

Reaction 3. $\Delta F.^\circ = 2{,}530 + 3.87\ T \log T - 0.782\times10^{-3}\ T^2 - \frac{0.932\times10^5}{T} - 9.09\ T.,$

Reaction 4. $\Delta F.^\circ = 195 + 11.205\ T \log T - 1.869\times10^{-3}\ T^2 - \frac{2.668\times10^5}{T} - 48.192\ T.$

Reaction With Methane

The rate of reaction between sulfur dioxide and methane is rather small when compared with its reduction with hydrogen or carbon monoxide. The reduction with methane requires higher temperatures.

In the presence of a bauxite catalyst at 900° C., methane and sulfur dioxide react to form sulfur, hydrogen sulfide, water, and carbon dioxide. At 800° C. conversion of methane is incomplete, and at 700° C. the reaction proceeds very slowly. At temperatures higher than 900° C., hydrogen and carbon monoxide are also formed. At 900° C. and a ratio of $CH_4:SO_2$ of 0.43 the yield of sulfur is 89.2 to 96.5 percent (249).

The course of the reaction between methane and sulfur dioxide was investigated in a quartz tube filled with pieces of quartz (252). Carbonyl sulfide is first formed according to:

$$2CH_4 + 3SO_2 = 2COS + 1/2S_2 + 4H_2O.$$

Carbonyl sulfide decomposes:

$$2COS = S_2 + 2CO,$$

$$2COS = CS_2 + CO_2.$$

The carbon monoxide that is formed reduces the sulfur dioxide,

$$2SO_2 + 4CO = 4CO_2 + S_2.$$

[6/] K_4 calculated from free-energy data in reference 208.

Original from THE OHIO STATE UNIVERSITY

From 800° to 850° C. large quantities of COS and CS_2 are formed; above 900° C., COS predominates owing to its re-forming from sulfur and carbon monoxide. COS was found at the highest temperature employed (1,150° C.) (252).

Walker (233) was able to suppress the formation of elementary sulfur and COS and increase the yield of hydrogen sulfide by using calcium sulfide as catalyst and operating with a ratio of $SO_2:CH_4$ of 0.5 at 850° to 1,000° C.

Thermodynamics:

In calculating the reduction equilibrium of sulfur dioxide and methane, the following equilibria must be considered:

$$CH_4 + 2SO_2 = CO_2 + 2H_2O + S_2; \qquad K_1 = (CO_2)\ (H_2O)^2\ (S_2)\ /\ (CH_4)\ (SO_2)^2;$$

$$4CO_2 + S_2 = 4CO + 2SO_2,$$

$$4H_2O + S_2 = 4H_2 + 2SO_2,$$

$$2H_2 + S_2 = 2H_2S,$$

$$2CO + S_2 = 2COS,$$

$$2COS = CO_2 + CS_2.$$

Temperature ...... °C.	25	400	500	600	800	1,000	1,200
log K_1 (13)	24.3	14.8		13.1	12.0		
log K_1 (249)			14.16	13.35	12.09	11.20	10.51

Free energy (249):

$$\log K_1 = -\frac{\Delta F^\circ}{4.58T}$$

	500° C.	600° C.	800° C.	1,000° C.	1,200° C.
-△ F.° in kcal.	50.08	53.31	59.38	65.25	70.83

Commercial Processes Employing Methane or Hydrocarbon Gases in Reducing Sulfur Dioxide

The Thiogen process (245) was carried out on a pilot-plant scale at Balakalla smelter, California, 1909 to 1911, and the Asarco process (57) on a semicommercial scale was operated by the American Smelting and Refining Company in Garfield, Utah.

Thiogen Processes (245)

Dry Process

Principle: Calcium, barium, or magnesium sulfate are reduced readily by hydrocarbon vapors at elevated temperatures to the sulfide; the latter is converted back to the sulfate by sulfur dioxide with the formation of free sulfur.

$$CaSO_4 \xrightarrow{CH_4} CaS \xrightarrow{SO_2} CaSO_4 + 2S.$$

Thus, if sulfur dioxide mixed with hydrocarbon vapors is passed through a combustion tube, reduction of sulfur dioxide takes place readily, and the products formed are sulfur, carbon dioxide, and water vapor.

When experiments were conducted at the plant, plaster of paris was dried, broken into lumps, and placed on a hearth. The mass was heated with oil burners. Roaster gases and oil vapors were then admitted. Because the roaster gases were not preheated, cooling of the hearth occurred, and the reaction stopped. Unfortunately, because of financial reasons further experiments to correct this difficulty were not undertaken. Young (245), however, makes these comments on the dry process:

(1) Reaction between sulfur dioxide and hydrocarbon gases is rapid.

(2) The method does not work well when the sulfur dioxide content is less than 7 percent. At lower percentages, sooting occurs on the "contact mass," and it is soon put out of commission.

(3) Preheating the gas is necessary.

Wet Process

The general procedure in the wet process is as follows:

(1) The sulfur dioxide is first absorbed by water in absorption towers.

(2) The aqueous solution of sulfur dioxide is reacted with a paste or solution of a suitable sulfide, such as barium sulfide. Considerable free sulfur, and, in addition, sulfites, thiosulfates, and thionates of barium are formed.

(3) The remaining sludge, containing free sulfur and the sulfur salts of the metal used, is filtered. The supernatant liquid is virtually pure water, which may again be returned to the absorption towers.

(4) The solids of the sludge, after settling and filtering, are dried and then raised to 450° to 500° C. In this way the complex sulfur salts are broken down, and the total sulfur available as free sulfur is distilled off and condensed. The still residue consists of a mixture of sulfite and sulfate with some sulfide. The sulfide is formed as a result of the breakdown of sulfites into sulfides and sulfates at higher temperatures.

(5) The residual sulfites and sulfates are next passed through a furnace, where they are reduced with hydrocarbon vapors to sulfide, which can then be brought back into reaction with further quantities of sulfur dioxide solutions (2).

Barium sulfide is preferred to the much less expensive calcium sulfide for several reasons:

(1) Barium sulfide is readily soluble in water, but calcium sulfide is not.

(2) The sulfur compounds of barium, resulting from the reaction of the barium sulfide with sulfur dioxide, are more insoluble than the corresponding compounds of calcium and crystallize in the anhydrous form while the calcium salts are hydrated.

(3) The settling and filtering properties of the barium sludge are superior to those of the calcium.

Asarco Process (57)

A high-purity sulfur (99.99 percent) has been prepared in a semicommercial plant of 5-ton-per-day capacity employing natural gas to reduce sulfur dioxide in smelter gases. A flowsheet of the process is shown in figure 10.

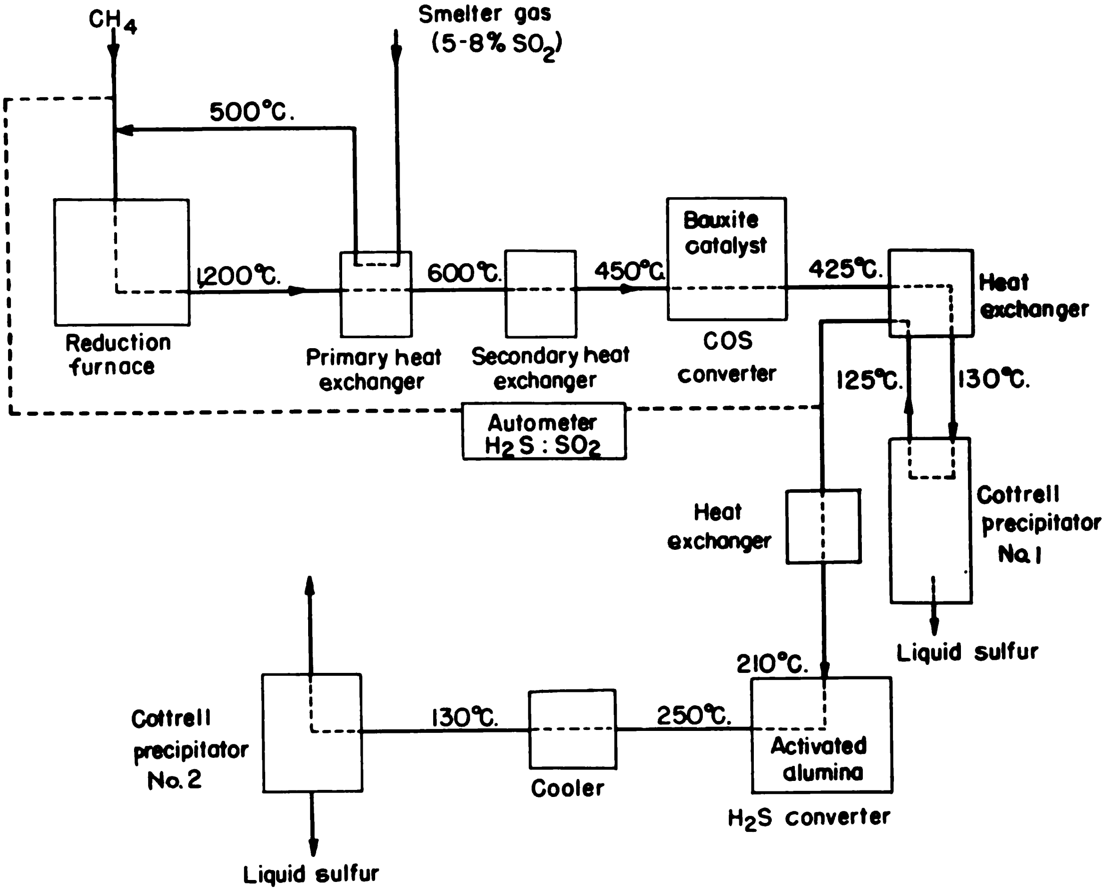


FIGURE 10. - Simplified Flow Diagram of Asarco Process. *(Reproduced From Fleming, E. P. and Fitt, T. C. (57).)*

The basic steps are:

Reduction: $2SO_2 + CH_4 \rightarrow 2H_2O + CO_2 + S_2$.

Several side reactions also take place, the chief products of which are COS and H_2S.

COS conversion: $2COS + SO_2 \rightarrow 2CO_2 + 3/2S_2$.

Gases leaving Cottrell precipitator No. 1 should contain 2 parts of hydrogen sulfide to 1 part of sulfur dioxide. If the proportion of hydrogen sulfide is too high, the natural-gas flow to the plant is reduced.

H_2S conversion: $2\ H_2S + SO_2 \rightarrow 2H_2O + 3/2S_2$.

The process is applicable for treating gases containing 5 to 8 percent sulfur dioxide by volume. A portion of the natural gas reacts with the excess oxygen to raise the temperature of the reactants in the furnace to 1,250° C. If the smelter gas contains over 8 percent sulfur dioxide there would be an oxygen deficiency, and a preheat of more than 500° C. would be necessary.

REDUCTION OF SULFUR DIOXIDE WITH CARBON

Dried sulfur dioxide gas reacts with carbon in the temperature range of 500° to 1,200° C. to form a mixture of carbon disulfide, carbonyl sulfide, sulfur, carbon monoxide, and carbon dioxide. The composition of the product varies, depending upon the temperature of the reaction and the nature of the carbon (178, 10). In the presence of moisture hydrogen sulfide is also produced.

Lepsoe (131) investigated the reaction on a laboratory and plant scale for producing sulfur using coke; Siller (208) studied the formation of carbon disulfide, using anthracite.

Formation of Sulfur (131)

In the reduction of sulfur dioxide by carbon the simultaneous reduction of carbon dioxide occurs. The simultaneous reactions are as follows:

$$SO_2 + C = CO_2 + 1/2S_2, \qquad (1)$$

$$CO_2 + C = 2CO. \qquad (2)$$

From the experimental data it would appear that between 900° and 1,200° C. reaction (2) is one-tenth as rapid as reaction (1). Actually the reduction of carbon dioxide is one-fifth that of the sulfur dioxide reduction. It is evident that a third reaction must occur:

$$SO_2 + 2CO = 2CO_2 + 1/2S_2. \qquad (3)$$

Lepsoe estimates that the sulfur dioxide reduction is diffusion controlled above 1,200° C.; the carbon dioxide reduction is diffusion controlled above 1,400° C.

In the laboratory studies dry sulfur dioxide was passed through calcined metallurgical coke (Michel coke containing 85 percent fixed carbon and 15 percent ash). Almost complete reduction of sulfur dioxide to sulfur was obtained in the temperature range 850°-1,200° C. At the higher temperatures shorter contact times were required.

Plant-scale operation: In the reduction of sulfur dioxide with carbon the exothermic heat of reaction (1) is 10,240 kcal. Reaction (2) required 41,530 kcal. In practice the two must be controlled to the extent that the exit gas carried enough carbon monoxide to combine with the residual sulfur dioxide in a subsequent catalytic reaction step (3). This condition is attained at or above a reduction degree of 0.90. The maximum combined heat is (0.90 x 10,240) - (0.13 x 41,530) or 3,800 kcal. per mole of sulfur dioxide reduced. This amount of heat is not enough to support the reaction, which, in order to attain the rate required for practical operations, must be carried out at temperatures well above 1,000° C. Extraneous heat must be added, and the simplest method is to introduce oxygen for the exothermic combustion of carbon.

Sulfur dioxide reduction and producer gas operation show marked similarity. Both depend on oxygen (air) for heat. On the other hand, the extent of the hot zone in the sulfur dioxide reduction is greater than in the gas producer operating on coke. To maintain high reduction rates and smooth operation, the temperature of the hot zone should not be less than 1,300° C.

Carbon consumption: The quantity of carbon consumed depends on the quantity of oxygen used. When minimum quantities of oxygen (11.1 percent) are used, the carbon consumption is 0.41 ton per ton of sulfur. When air instead of oxygen is used the carbon consumption is 0.44 ton. These are minimum figures. Actual carbon consumption would be higher depending on the quantity of carbon lost in the coke ash and the efficiency of catalysis. Coke is the major factor in the cost of sulfur dioxide reduction.

Reactivity of coke: Metallurgical cokes vary in reactivity. Inorganic constituents, particularly iron, have an effect on reactivity. Iron in the metallic state or in a form easily reducible to the metallic state has a marked effect in enhancing the reactivity (109). The high reactivity of nonmetallurgical coke is due largely to the presence of hydrocarbons. It may be inferred that reduction with carbonaceous materials having more than 100 times the reactivity of metallurgical coke is not brought about by carbon but by unsaturated complex hydrocarbons. Coal as a reducing agent would have the advantage of lower cost than coke and would require a much lower ignition temperature. The disadvantage of coal is the copious production of hydrogen sulfide, which is much more difficult to catalyze completely than carbon monoxide or oxysulfide.

The thermodynamics of the reduction of sulfur dioxide is discussed by Lepsoe (130) in an earlier work.

Formation of Carbon Disulfide

Siller (208) has shown that, when sulfur dioxide is passed through a bed of anthracite, carbon disulfide rather than sulfur was formed when the middle of the bed was kept hotter than the ends. When the bed was at uniform temperature (900° to 1,000° C.) low carbon disulfide yields (5 to 15 percent) were obtained. When the temperature in the middle was increased to 1,100° to 1,200° C. and that of the bottom lowered to 500° to 700° C., while the top was maintained at 900° to 1,000° C., the carbon disulfide yield increased (up to 67 percent), and very little sulfur was detected. As the temperature of the middle section was increased, the carbonyl sulfide content of the offgases decreased, and the carbon monoxide content increased. When the sulfur dioxide was diluted with nitrogen ($9SO_2:91N_2$), a very high carbon disulfide yield was obtained (90 percent).

Postulated mechanism of the process: The reaction is believed to take place in three steps.

Step 1. - The chief product in the lower part of the furnace (500° to 700° C.) was carbonyl sulfide by the rapid reaction:

$$3C + 2SO_2 = 2COS + CO_2. \qquad (1)$$

As the carbon dioxide passed to the hotter portions of the coal column, it was converted to carbon monoxide:

$$CO_2 + C = 2CO. \qquad (2)$$

The result of adding equations (1) and (2) was

$$4C + 2SO_2 = 2COS + 2CO. \qquad (3)$$

Step 2. - Carbonyl sulfide reaching the hot middle part of the bed is dissociated.

$$2COS = 2CO + 2S. \qquad (4)$$

Step 3. - The atomic sulfur formed in (4) in the presence of the hot coal is is highly reactive.

$$C + 2S = CS_2. \qquad (5)$$

The overall process:

$$\begin{array}{ll} 4C + 2SO_2 = 2COS + 2CO, & (3) \\ 2COS = 2CO + 2S, & (4) \\ \underline{C + 2S = CS_2.} & (5) \\ 5C + 2SO_2 = CS_2 + 4CO. & (6) \end{array}$$

Reaction (6) is endothermic and requires 62,980 calories to produce 1 mole of carbon disulfide. The heat derived from burning 4 moles of carbon monoxide is 270,480 calories or 4.3 times the quantity necessary to form 1 mole of carbon disulfide. The process could be self-sustaining by using the byproduct carbon monoxide as fuel for heating the reaction tube but not if roaster gases are used directly as a source of sulfur dioxide. The calorific value of the gas would be low because of the dilution with nitrogen.

The type of carbon used in the process is important. When metallurgical coke was substituted for anthracite, very little CS_2 was formed. In addition to having a greater initial reactivity than coke, anthracite was continually activated by the chemical reactions that took place in the process. It is virtually impossible to activate graphitic carbon.

The reader is referred to several patents on preparing carbon disulfide from sulfur dioxide (23, 44, 144).

Thermodynamics:

A more recent and rigorous thermodynamic treatment of the formation of carbon disulfide from carbon is presented by Owen and others (167).

The yield of CS_2 from carbon and sulfur dioxide increases with temperature; at lower temperatures a considerable part of sulfur dioxide becomes COS.

Product	Conversion of SO2, percent		
	1,000° K.	1,200° K.	1,400° K.
CS_2	37.08	68.88	81.16
COS	59.70	23.42	8.02
S_2	3.22	7.07	10.82

The heat absorbed per mole of CS_2 formed at equilibrium, kcal.:

1,000° K.	1,200° K.	1,400° K.
57	75	72

Equilibrium constants:

		1,000° K.	1,200° K.	1,400° K.
$2COS = 2CO + S_2$	$K = (CO)^2(S_2)/(COS)^2$	0.0208	0.881	12.6
$C + S_2 = CS_2$	$K = (CS_2)/S_2)$	11.5	8.97	7.48
$S_2 + 2CO = 2COS$	$K = (COS)^2/(S_2)(CO)^2$	48.1	1.13	.0792
$SO_2 + 2C = COS + CO$	$K = (COS)(CO)/(SO_2)$	3.35×10^6	8.45×10^6	16.1×10^6
$2COS = CO_2 + CS_2$	$K = (CO_2)(CS_2)/(COS)^2$	.116	.130	.142

OXIDATION OF SULFUR DIOXIDE

Use of Air

Sulfur dioxide is oxidized by air at atmospheric temperatures to the trioxide, but the rate and subsequently the yield is low. The reaction is exothermic, liberating 44 kilocalories per mole of oxygen consumed. Although the equilibrium is not favored, the rate of reaction increases as the temperature rises. The maximum combination of sulfur dioxide and oxygen occurs at 425° to 450° C. in the presence of a contact catalyst such as platinum or vanadium oxide.

$$2SO_2(g) + O_2 \rightleftarrows 2SO_3(g) \quad \Delta H_{298.1} = -43{,}800 \text{ calories } (\underline{115}),$$

$$\Delta H = -43{,}200 - 2T.$$

Equilibrium constants:

$$Kp = \frac{P_{SO_3}}{P_{SO_2} . P_{O_2}^{1/2}} \qquad P = \text{partial pressure (atmospheres)}$$

$$Kc = \frac{C_{SO_3}}{C_{SO_2} . C_{O_2}^{1/2}} \qquad C = \text{concentration (gm. moles/liter)}$$

The fairly reliable data reported by Bodenstein and Pohl (14):

Temperature, °C.	Kc	Kp
528	254	31.33
579	114.3	13.67
627	56.26	6.546
680	29.88	3.378
727	16.81	1.856
789	8.909	0.9543
832	5.976	0.6276
897	3.501	0.3573

At lower temperatures from Knietsch (119), as tabulated by Gmelins (83):

Temperature, °C.	Kc	Kp
430	1,917	252.4
460	1,000	128.9
470	671	85.94
490	471	59.52

An approximate equation for the dependence of the equilibrium constant upon temperature is given for $K_c' = \frac{C^2_{SO_3}}{C^2_{SO_2}.C_{O_2}}$ where $K_c' = (K_c)^2$ (14).

$$\log_{10}K_c = \frac{10,373}{T} + 2.22 \log_{10}T - 14.585, \quad T = \text{absolute temperature},$$

$$\Delta F° = -21,600 + 2.305\ T \log T + 13.44\ T \ (115).$$

Contact Process

Sulfuric acid is manufactured mostly by the contact process, although as late as 1900 no contact plant had been built in the United States. For a review the reader is referred to the works of Miles (148) and Fairlie (50).

Burner gas, containing about 7 to 8 percent sulfur dioxide, 9 percent oxygen, and the remainder nitrogen, is obtained from a variety of raw materials - sulfur, iron pyrites, waste gases from copper smelters, and spent oxides from purifying coal gas. The burner gases are scrubbed to remove impurities that would poison the catalyst. Arsenic and halogens, even in minute quantities, render a platinum catalyst inactive; the oxides of iron and vanadium are less sensitive to these poisons. For an excellent discussion of contact catalysts see Fairlie (50). Recently the trend has been almost completely to the use of vanadium oxide as the catalyst (123).

The purified burner gases enter the converter at about 410° C. and are heated by the exothermic reaction to 600° C., resulting in about 70 percent conversion of the sulfur dioxide. The gas is then cooled in a heat exchanger or in a waste-heat boiler until the temperature is around 430° C., after which the gas contacts additional catalyst. The final yield of sulfur trioxide is over 97 percent.

The sulfur trioxide from the converter gas cannot be absorbed by passing through water, as a dense fog of minute droplets of sulfuric acid is formed. The gas is passed into 97- to 99-percent sulfuric acid in iron scrubbing towers. The concentrated acid rapidly absorbs the sulfur trioxide, producing fuming sulfuric acid or oleum.

Figure 11 is a flowsheet of a contact-acid plant of the Monsanto Chemical Co., using sulfur as a raw material and vanadium pentoxide as catalyst (113).

Air rather than oxygen has been used in all contact plants. Substitution of oxygen would decrease the size of equipment and eliminate waste gases to the atmosphere. However, higher temperatures would require more expensive equipment in the sulfur burner and in the converter. A single installation using pure oxygen has been made at the Consolidated Mining & Smelting Co., Trail, British Columbia (213).

The five principal types of contact plants (50) are:

1. The Badische process (119).
2. The Grillo-Schroeder process.
3. The Mannheim process - obsolete, of historical interest.
4. The Tentelew process - obsolete, of historical interest.
5. Chemico-Brimstone - developed by the Chemical Construction Corp., 1927.

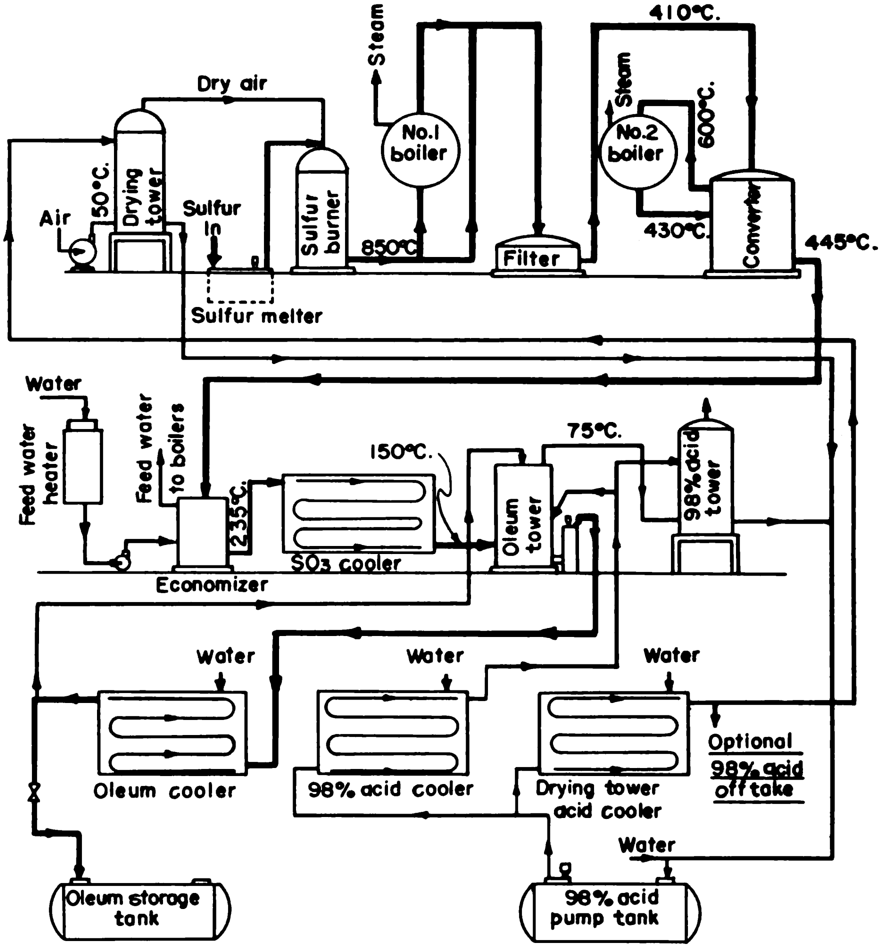


FIGURE 11. - Flowsheet of Monsanto Contact Acid Plant. *(Reproduced From Kastens, M. L. and Hutchinson, J. C. (113).)*

A new plant was built by the Chemical Construction Corp. at Hamilton, Ohio, in 1950; its features represent the first real change in the contact-acid process in over 50 years. A marked increase in conversion efficiency, a 90-percent or more reduction in cooling-water requirements, a greatly simplified plant, and a decrease in investment and physical size of the plant are reported (165). The reader is referred to a discussion of the methods for recovering sulfur dioxide from the tail gases of contact sulfuric acid plants in Great Britain (102).

Use of Ozone

Sulfur dioxide reacts almost quantitatively with ozone below 46° C., the boiling point of sulfur trioxide, when roaster gases or mixtures of sulfur dioxide and air are subjected to the action of electric sparks (186). The reaction is
$3SO_2 + O_3 \rightarrow 3SO_3$.

Anhydrous sulfur dioxide reacts very slowly with ozone; in the presence of water vapor, yields are high. When the excess of sulfur dioxide is large and the ozone is dilute, there is extensive participation of oxygen in the reaction. A yield of 194 percent sulfur trioxide (based on the quantity of ozone) was observed when the oxygen contained 1 percent ozone and the sulfur dioxide amounted to about 8 times the equivalent of ozone (19).

EFFECT OF HEAT ON SULFUR DIOXIDE

The thermal dissociation of sulfur dioxide is very slight, and perceptible amounts of dissociation products are observed only at very high temperatures (198, 253).

$$SO_2 = O_2 + 1/2S_2 \text{ (g)}, \qquad (1)$$

$$SO_2 = 1/2O_2 + SO. \qquad (2)$$

$$K_1 = \frac{SO_2}{(S_2)^{1/2}(O_2)} \qquad K_2 = \frac{SO_2}{(SO)(O_2)^{1/2}}$$

Temperature, °K.	$\log_{10}K_1$	Dissociation of SO_2, percent	$\log_{10}K_2$	Dissociation of SO_2, percent
298.1	59.73	1.9×10^{-38}	54.61	4.9×10^{-35}
400	43.56	1.1×10^{-27}	39.68	4.4×10^{-25}
600	27.78	3.8×10^{-17}	25.09	2.4×10^{-15}
800	19.88	7.0×10^{-12}	17.80	1.7×10^{-10}
1,000	15.14	1.0×10^{-8}	13.42	1.4×10^{-7}
1,200	11.99	1.3×10^{-6}	10.50	1.3×10^{-5}
1,400	9.73	4.1×10^{-5}	8.41	3.1×10^{-4}
1,600	8.04	5.5×10^{-4}	6.85	3.4×10^{-3}
2,000	5.68	2.1×10^{-2}	4.67	9.7×10^{-2}
2,400	4.10	2.3×10^{-1}	3.21	9.1×10^{-1}
2,800	2.98	1.3	2.17	4.5

The thermal dissociation of sulfur dioxide into sulfur and sulfur trioxide is also very slight. At 900° C. the equilibrium constant, K, for the reaction

$$6SO_2 = 4SO_3 + S_2; \quad \Delta H = -71 \text{ kcal.}$$

is 2.5×10^{-22} (161). For the thermal dissociation of sulfur dioxide in the presence of platinum see page 17.

EFFECT OF LIGHT ON SULFUR DIOXIDE

Sulfur dioxide is decomposed at atmospheric pressure by ultraviolet light from a quartz-mercury lamp into sulfur trioxide and sulfur, $3SO_2 = 2SO_3 + S$; in the presence of oxygen the reaction is $2SO_2 + O_2 = 2SO_3$. Both reactions, however, failed to take place when the gases were dried over P_2O_5 (30).

Dissociation of Sulfur Dioxide

No dissociation of sulfur dioxide into sulfur and sulfur trioxide was obtained with light of wavelength 2,537A. Dissociation was obtained at lower wavelengths. Quantum efficiencies (molecules reacting per quantum absorbed) were 1.00 at 1,860A, 0.71 at 2,070A, 0.53 at 2,200A and <0.01 at 2,537A (122).

At room temperature the absorption spectrum of gaseous sulfur dioxide in the ultraviolet consists of 2 band systems, 1 between 2,600 and 3,900A, the other between

1,700 and 2,400A. At 450° C. the bands due to sulfur dioxide disappear, and a spectrum due to sulfur appears. Upon cooling, the sulfur dioxide bands reappear with the same intensity as before heating (239).

Oxidation of Sulfur Dioxide

Coehn and Becker investigated the effect of ultraviolet light upon the reaction $2SO_2 + O_2 = 2SO_3$. The equilibrium constant, $K = \frac{(O_2)(SO_2)^2}{(SO_3)^2}$, was independent of the proportion of sulfur dioxide and oxygen present and of the temperature (room temperature to 800° C.). Decreasing the intensity of light caused equilibrium constant K to decrease. Some experiments on possible commercial manufacture of sulfur trioxide by means of ultraviolet light are described. A temperature of 450° C. or higher is necessary to have sufficiently rapid reaction. When the excess of oxygen was ninefold, a yield of over 90 percent sulfur trioxide was obtained. The presence of nitrogen did not interfere (31).

The reader is directed to other references on the dissociation of sulfur dioxide (63, 96, 121) and on the oxidation of sulfur dioxide (120, 226).

EFFECT OF AN ELECTRIC DISCHARGE ON SULFUR DIOXIDE

When Berthelot's apparatus was used, a silent electric discharge through sulfur dioxide produced sulfur and sulfur trioxide, $3SO_2 = 2SO_3 + S$ (132).

Sulfur dioxide in a discharge tube was subjected to an alternating current, 50 cps., 4 to 16 kilovolts and current of <0.1 ma. After the reaction, rapid at first, dropped and finally reached equilibrium, increase in the voltage had no effect. The resulting mixture consisted of 10 percent undissociated SO_2, SO_3, O_2, and 2 species of unidentified solids deposited in small quantities near the electrodes (110).

Mixtures of sulfur dioxide and oxygen were oxidized to sulfur trioxide on exposure to an electrodeless discharge. No thionates or polythionates were found in the products. The results indicated that a maximum quantity of sulfur dioxide is oxidized when the mixture has a composition of 60 percent sulfur dioxide and 40 percent oxygen. The oxygen is activated by the discharge and combines with the sulfur dioxide (136).

When a mixture of hydrogen and sulfur dioxide was subjected to a silent electric discharge of 6.7 kilovolts, the reaction products consisted of S, H_2SO_3, H_2SO_4, SO_3, O_2, O_3, and H_2S (41).

Technical Applications in Using Electric Discharge

Air-sulfur dioxide mixtures have been exposed to electric fields of high voltage (25 to 50 kilovolts), low amperage (~5 ma.) and of varying frequencies for converting sulfur dioxide to sulfur trioxide. These methods have been the subject of many patents (4, 33, 37, 164, 220, 223). Glockler and Lind discuss the use of ozonizers, silent, glow, and spark discharges and other aspects of the electrochemistry of gases (82).

The U.S.S.R. claims to have successfully oxidized sulfur dioxide in flue gases in a silent electric discharge; removal of the resulting sulfur trioxide mist was accomplished by electrostatic precipitation (183).

DECOMPOSITION OF SULFATES

Sulfates may be decomposed by several methods - thermal decomposition, electrolysis, or reduction with hydrogen.

Thermal Dissociation

The thermal decomposition of sulfates and their hydrates in a current of air has been reported by Hofman and Wanjukow (98). The temperatures reported are lower for the same degree of dissociation than if the compound was heated in an evacuated tube and in equilibrium with its atmosphere of dissociation products. While the latter method would give the true equilibrium pressure of the gaseous products as a function of temperature, the results of Hofman and Wanjukow are an important contribution in the recovery of sulfur dioxide. If a sulfate was formed through reaction of an oxide with sulfur dioxide, thermal dissociation in the presence of a flowing stream of air might be an effective means of regeneration. Lower temperatures would result, and the effluent gas - sulfur dioxide, sulfur trioxide, and air - could then be sent to a contact unit.

Manganese sulfate: In a current of air the dissociation of manganese sulfate is as follows (98):

$$MnSO_4 \cdot 5H_2O \xrightarrow{25^\circ\text{ C.}} MnSO_4 \cdot 2H_2O \xrightarrow{60^\circ\text{ C.}} MnSO_4 \cdot H_2O \xrightarrow{152^\circ\text{ C.}} MnSO_4 \xrightarrow{\text{7/}\,699^\circ\text{-}790^\circ\text{ C.}} Mn_3O_4.$$

$MnSO_4 \cdot 5H_2O$	$MnSO_4 \cdot 2H_2O$	$MnSO_4 \cdot H_2O$	$MnSO_4$	Mn_3O_4
Peach blossom	Pale peach blossom	Paler	Paler	Dark red to black

The equilibrium dissociation of manganese sulfate is reported by Marchal (141).

$$3MnSO_4 \rightarrow Mn_3O_4 + 2SO_3 + SO_2.$$

Temperature, °C.	Dissociation pressure, mm. Hg.
800	18.3
1,000	527
1,100	2,000

Magnesium sulfate: In a current of air the dissociation of magnesium sulfate is as follows (98):

$$MgSO_4 \cdot 7H_2O \xrightarrow{19^\circ\text{ C.}} MgSO_4 \cdot 6H_2O \xrightarrow{38^\circ\text{ C.}} MgSO_4 \cdot 2H_2O \xrightarrow{112^\circ\text{ C.}} MgSO_4 \cdot H_2O \xrightarrow{203^\circ\text{ C.}} MgSO_4$$

$MgSO_4 \cdot 7H_2O$	$MgSO_4 \cdot 6H_2O$	$MgSO_4 \cdot 2H_2O$	$MgSO_4 \cdot H_2O$	$MgSO_4$
White	White	White	White	

$$MgSO_4 \xrightarrow{890^\circ\text{-}972^\circ\text{ C.}} MgO$$

$MgSO_4$	MgO
	White

Calcium sulfate: In a current of dry air the dissociation of calcium sulfate is as follows (98):

7/ This temperature may be compared with the value of 1,030° C. when $MnSO_4$ is heated in a tube closed at one end.

Original from THE OHIO STATE UNIVERSITY

$$\underset{\text{White}}{CaSO_4\cdot 2H_2O} \xrightarrow{30^\circ\text{-}77^\circ\text{ C.}} \underset{\text{White}}{CaSO_4\cdot H_2O} \xrightarrow{77^\circ\text{-}110^\circ\text{ C.}} \underset{\substack{\text{or}\\(2CaSO_4\cdot H_2O)\\\text{White}}}{CaSO_4\cdot 1/2H_2O} \xrightarrow{110^\circ\text{-}344^\circ\text{ C.}} \underset{\text{White}}{CaSO_4}$$

$$CaSO_4 \xrightarrow{\underline{8}/>1{,}200^\circ\text{ C.}} \underset{\text{White}}{CaO}$$

Copper sulfate: The thermal decomposition of copper sulfate in a current of dry air is as follows (98):

$$\underset{\text{Blue}}{CuSO_4\cdot 5H_2O} \xrightarrow{27^\circ\text{-}30^\circ\text{ C.}} \underset{\text{Sky blue}}{CuSO_4\cdot 3H_2O} \xrightarrow{93^\circ\text{-}99^\circ\text{ C.}} \underset{\text{Pale blue}}{CuSO_4\cdot H_2O} \xrightarrow{155^\circ\text{-}233^\circ\text{ C.}} \underset{\text{White}}{CuSO_4}$$

$$CuSO_4 \xrightarrow{\underline{9}/653^\circ\text{-}670^\circ\text{ C.}} \underset{\text{Orange}}{2CuO\ SO_3} \xrightarrow{702^\circ\text{-}736^\circ\text{ C.}} \underset{\text{Black}}{CuO.}$$

Iron sulfate: The thermal decomposition of iron sulfate in a current of dry air (98):

$$\underset{\text{Blue green}}{FeSO_4\cdot 7H_2O} \xrightarrow{21^\circ\text{ C.}} \underset{\substack{\text{Light}\\\text{apple green}}}{FeSO_4\cdot 4H_2O} \xrightarrow{80^\circ\text{ C.}} \underset{\text{White}}{FeSO_4.H_2O} \xrightarrow[\substack{\text{(An oxida-}\\\text{tion and}\\\text{dehydration}}]{167^\circ\text{-}455^\circ\text{ C.}} \underset{\substack{\text{Yellow}\\\text{brown}}}{Fe_2O_3\cdot 2SO_3} \xrightarrow{492^\circ\text{-}560^\circ\text{ C.}} \underset{\text{Red}}{Fe_2O_3.}$$

Lead sulfate: The thermal decomposition of lead sulfate in a current of dry air is as follows (98):

$$PbSO_4 \xrightarrow{195^\circ\text{-}705^\circ\text{ C.}} 6PbO\cdot 5SO_3 \xrightarrow{888^\circ\text{-}952^\circ\text{ C.}} Pb.$$

Zinc sulfate: The thermal decomposition of zinc sulfate in a current of dry air is as follows (98):

$$\underset{\text{White}}{ZnSO_4\cdot 7H_2O} \xrightarrow{25^\circ\text{ C.}} \underset{\text{White}}{ZnSO_4\cdot 6H_2O} \xrightarrow{28^\circ\text{ C.}} \underset{\text{White}}{ZnSO_4\cdot 2H_2O} \xrightarrow{115^\circ\text{ C.}} \underset{\text{White}}{ZnSO_4\cdot H_2O} \xrightarrow{225^\circ\text{ C.}} \underset{\text{White}}{ZnSO_4}$$

$$ZnSO_4 \xrightarrow{\underline{10}/702^\circ\text{-}720^\circ\text{ C.}} \underset{\text{White}}{3ZnO\cdot 2SO_3} \xrightarrow{755^\circ\text{-}757^\circ\text{ C.}} \underset{\substack{\text{White}\\\text{(yellow when hot)}}}{ZnO.}$$

8/ The presence of SiO_2 lowered the start of dissociation to 1,000° C. The velocity of thermal dissociation of calcium sulfate is strongly accelerated by the presence of water vapor (20).

9/ When heated in a tube closed at one end:

$$CuSO_4 \xrightarrow{740^\circ\text{ C.}} 2CuO\cdot SO_3 \xrightarrow{845^\circ\text{ C.}} CuO.$$

10/ When heated in a tube closed at one end:

$$ZnSO_4 \xrightarrow{840^\circ\text{ C.}} 3ZnO\cdot 2SO_3 \xrightarrow{935^\circ\text{ C.}} ZnO.$$

Original from THE OHIO STATE UNIVERSITY

Aluminum sulfate: The thermal decomposition of aluminum sulfate in a current of dry air is as follows (98):

$$\underset{\text{White}}{Al_2(SO_4)_3\cdot 16H_2O} \xrightarrow{51^\circ\text{ C.}} \underset{\text{White}}{Al_2(SO_4)_3\cdot 13H_2O} \xrightarrow{82^\circ\text{ C.}} \underset{\text{White}}{Al_2(SO_4)_3\cdot 10H_2O} \xrightarrow{97^\circ\text{ C.}} \underset{\text{White}}{Al_2(SO_4)_3\cdot 7H_2O} \xrightarrow{109^\circ\text{ C.}}$$

$$\underset{\text{White}}{Al_2(SO_4)_3\cdot 4H_2O} \xrightarrow{180^\circ\text{ C.}} \underset{\text{White}}{Al_2(SO_4)_3\cdot H_2O} \xrightarrow{316^\circ\text{ C.}} \underset{\text{White}}{Al_2(SO_4)_3}\text{[11]} \xrightarrow{590^\circ\text{-}639^\circ\text{ C.}} \underset{\text{White}}{Al_2O_3}.$$

Electrolysis of Metal Sulfates

This subject is presented under Electrolysis of Compounds Containing Sulfur (p. 46).

Hydrogen Reduction of Sulfates

Reduction of metallic salts in solution to the free metal can be carried out by the use of gaseous hydrogen.

$$M^{++} + H_2 \rightleftharpoons M^o + 2H^+$$

Figure 12 is a plot of the electrode potentials at 25° C. for 1 and 0.001 M concentrations of several metal ions, and also the hydrogen potential at various pH values at 1 and 100 atmospheres partial pressures. As the reduction proceeds the hydrogen-ion concentration increases, and the pH decreases; thus the potential for reduction by hydrogen decreases. With metals such as copper which are below hydrogen in the electromotive series, complete reduction has been obtained from sulfuric acid solutions as strong as 20 percent. When the metals are more electropositive, it is necessary to reduce the hydrogen-ion concentration by buffering and complex formation. Reduction of 10 percent of nickel when present as nickel sulfate can be effected before the solution becomes too acid. When ammonium sulfate was added the hydrogen ions produced were neutralized by formation of bisulfate ion. Thus, buffering allowed 50 percent of the nickel to be reduced before the solution became too acid. When ammonium acetate was added, the hydrogen ions were tied up largely as undissociated acetic acid, allowing 100-percent reduction of the nickel sulfate solution. These data are tabulated in table 1. Cadmium was the least noble of the metals to be precipitated in pure form at industrially satisfactory yields and rates (195).

TABLE 1. - Hydrogen reduction of various nickel solutions[1]

Solution	Approximate reduction at equilibrium, percent	Final pH, room temperature
$NiSO_4$	10	2.2
$NiSO_4$-$(NH_4)_2SO_4$	50	1.6
$NiSO_4$-NH_4 acetate ..	100	4.1

[1] Nickel 0.2 M, t = 200° C., hydrogen pressure, 1,000 p.s.i.g.

---

[11] When heated in a tube closed at one end:

$$Al_2(SO_4)_3 \xrightarrow{770^\circ\text{ C.}} Al_2O_3.$$

Original from THE OHIO STATE UNIVERSITY

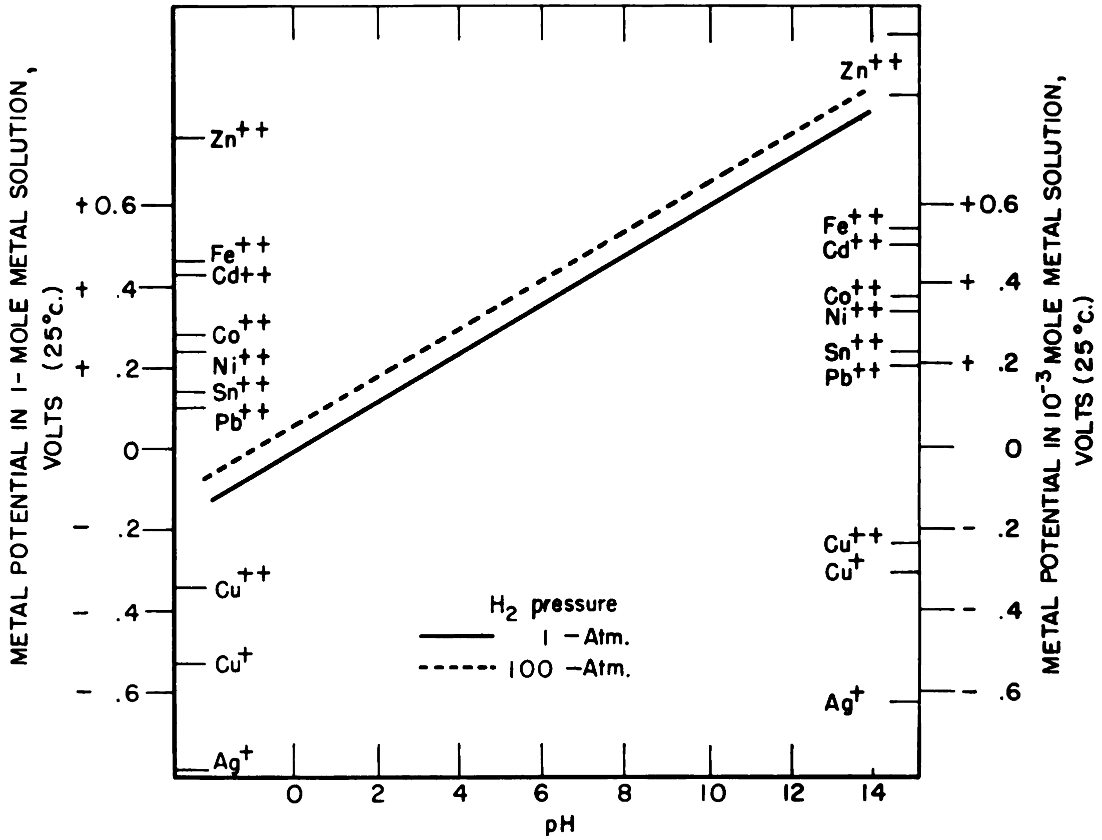


FIGURE 12. - Potential of 1 and 10^{-3} Molar Metal Solutions, and Hydrogen Potential at Varying pH (25° C.). *(Reproduced From Schaufelberger, F. A. (195).)*

ELECTROLYSIS OF COMPOUNDS CONTAINING SULFUR (76, 80)

Various types of sulfur compounds can be formed in the absorption of sulfur dioxide. Electrolysis may be employed as an intermediate step in their conversion to a more useful form. In a powerplant installation electrical energy for electrolysis would be readily available. A discussion of the electrolysis of several types of inorganic sulfur compounds follows.

Electrolytic Oxidation of Sulfides

In the electrolytic oxidation of sulfides the first product is undoubtedly sulfur, but if the solution of sulfide is reasonably concentrated it dissolves to form polysulfides,

$$S^{=} + S = S^{=}_{X+1},$$

where X+1 may have a value up to about 5, or slightly more. When the solution in the vicinity of the anode becomes saturated, free sulfur begins to separate on the electrode, and periodic fluctuations of current and potential are observed. For any sodium sulfide solution there is a certain limiting current density,[12] below which sulfur does not separate. When current density is not too high, the only product of electrolysis of Na_2S is sodium polysulfide; sulfate and dithionate ($S_2O_6^=$) are formed at high current densities, but no thiosulfate ($S_2O_3^=$) (52).

---

[12] Current density is equal to the current strength in amperes divided by the area of the electrode in square centimeters.

For polysulfide solutions of composition Na_2S_x the limiting current density increases at first in proportion to the sulfur in solution, passes through a maximum, and then decreases to zero (52).

When a solution of acid sodium sulfide (NaSH) is electrolyzed, polysulfide and hydrogen sulfide are formed in the ratio of $1Na_2S_2 : 2H_2S$ (52).

Oxidation of Sulfurous to Sulfuric Acid

The electrolytic oxidation of sulfurous acid is of interest because of its possible use as a method for manufacturing sulfuric acid in removing sulfur dioxide from flue gases.

If an aqueous solution containing sulfur dioxide is electrolyzed, sulfuric acid is formed at the anode. Fischer and Delmarcel (55) found that a 1- to 5-percent solution of sulfur dioxide could be readily oxidized. Thompson and Thompson (221) used an electrolyte of sulfuric acid into which sulfur dioxide was bubbled beneath a platinum anode. They concluded that sulfurous acid could be readily oxidized to sulfuric acid to a concentration up to 95 percent.

More recently the reaction of sulfur dioxide, water, and oxygen in an electrolytic cell to form sulfuric acid was studied (203).

$$SO_2 + 1/2O_2 + H_2O = H_2SO_4;$$

$$\Delta H_{25^\circ\ C.} = -52{,}100 \text{ calories,}$$

$$\Delta F_{25^\circ\ C.} = -49{,}100 \text{ calories.}$$

To utilize this energy and simultaneously produce sulfuric acid, the foregoing reaction was allowed to take place in a gas cell with platinum electrodes. However, many obstacles must be overcome before a cell can be devised to generate an electric current and simultaneously produce sulfuric acid from sulfur dioxide, oxygen, and water.

Electrolytic Oxidation of Thiosulfates

The main product in the electrolytic oxidation of thiosulfate is tetrathionate,

$$2\ S_2O_3^= = S_4O_6^=,$$

but a small quantity of sulfate is formed. The proportion of the latter increases as the pH of the solution is increased. The anodic oxidation of thiosulfate is regarded as a secondary chemical reaction and not as an electrochemical process involving the discharge of thiosulfate ions. Glasstone (81) postulated a hydrogen peroxide theory for the anodic oxidation of thiosulfate as follows: First is the discharge of hydroxyl ion from water, which is a slow process,

$$H_2O = OH + H^+ + e,$$

followed by

$$2OH = H_2O_2,$$

and $2S_2O_3^= + H_2O_2 = S_4O_6^= + 2OH^-$,

or $S_2O_3^= + OH = S_2O_3^- + OH^-$,

and $2S_2O_3^- = S_4O_6^=$.

The addition to the electrolyte of catalysts for decomposing hydrogen peroxide (for example ferrous, copper, cobalt, and manganese salts) results in decreased efficiency of the formation of tetrathionate. A 0.001 M solution of $MnSO_4$ is capable of preventing entirely the electrolytic oxidation of 0.025 M sodium thiosulfate (77). The yield of sulfate may be increased by the presence of molybdic acid (78).

Electrolytic Oxidation of Sulfites

Foerster and Friessner (59) noted that, in the electrolysis of sodium sulfite solutions, no oxygen escaped at the anode, but that dithionate ($S_2O_6^=$) and sulfate were formed. The electrolysis was more thoroughly investigated by Glasstone (79). The chief products are sulfate and dithionate. The proportion of the latter is increased by previous anodic polarization of the electrode and decreased by cathodic treatment. In acid solution very little dithionate is formed. As the pH is increased, the yield of dithionate increases until a maximum is obtained at a pH of 8; thereafter the yield decreases. If catalysts that decompose H_2O_2 are added to the electrolyte, a marked decrease in the proportion of dithionate and an increase in sulfate content result. Glasstone (79) proposes that the oxidation of sulfite to dithionate, $2SO_3^= = S_2O_6^=$, is similar to the oxidation of thiosulfate to tetrathionate, a chemical rather than an electrochemical process, proceeding by the hydrogen peroxide mechanism.

Electrolysis of sulfates

Electrolysis of Sulfuric Acid (80)

The electrolytic oxidation of sulfuric acid is accompanied by evolution of some oxygen and ozone and formation of $H_2S_2O_8$ (perdisulfuric or more simply persulfuric acid) and H_2SO_5 (permonosulfuric or Caro's acid) and a small quantity of H_2O_2.

Electrolysis of Metal Sulfates

Alkali metals: The electrolysis of alkali metal sulfates is not as complex as that of sulfuric acid. As the persulfates of potassium and ammonium are sparingly soluble in acid solution, the concentration of persulfate is small; consequently, little permonosulfuric acid forms even in strongly acid electrolytes. Ammonium sulfate is particularly suitable for persulfate formation, since the sulfate is very soluble, and in acid solution the persulfate readily separates out. The production of ammonium persulfates has been described (235).

Polyvalent metals: Whereas the alkali sulfates behave similarly to the free acid on electrolysis, many polyvalent metals follow a different course. On electrolysis ferrous sulfate yields ferric sulfate, and cobaltous sulfate is oxidized to cobaltic sulfate. Other metals hydrolyze to higher valence states. Chromic sulfate is oxidized to the 6-valence state - the resulting sulfate then hydrolyzing to sulfuric and chromic acids. Manganous sulfate is oxidized to the 3-, 4-, and 7-valence states; hydrolysis of the last 2 sulfates results in formation of manganese dioxide and permanganic acid along with sulfuric acid. The choice of conditions will determine whether the oxide is precipitated or the permanganic acid forms (48).

Manganous Sulfate

Berthelot (9) observed that in the electrolysis of a dilute solution of manganous sulfate using a very weak e.m.f., manganese dioxide is precipitated along with the formation of sulfuric acid at the anode, and hydrogen is liberated at the cathode. Oxygen does not appear at the anode, nor is metallic manganese liberated at the cathode.

Frei (64) observed that in the electrolysis of manganous sulfate when the acid concentration is low, manganese dioxide is formed; when the concentration of acid is larger, manganese remains in solution. The quantities, in grams per 100 cubic centimeters, of sulfuric acid, which prevent the separation of manganese dioxide from solutions of various concentrations, are as follows:

$MnSO_4$/liter .... mole		0.01	0.02	0.10	0.15	0.20	0.50	1.00
H_2SO_4 .... gm./100 cc.	16° C.	3.5	16.5	40.0	40.5	39.5	34.0	29.0
	60° C.	27.0	37.0	59.0	59.0	58.0	54.0	45.0
	80° C.	44.0	54.0	70.5	58.3	68.5	58.0	-

A low temperature is favorable for formation of permanganate.

Manganese electrode potentials in acid solution may be summarized as follows (127):

$$\begin{tikzcd}[column sep=large]
Mn \arrow[r, dash, "+1.18"] & Mn^{++} \arrow[r, dash, "-1.51"] \arrow[rr, dash, bend right, "-1.23"'] & Mn^{+++} \arrow[r, dash, "-0.95"] & MnO_2 \arrow[r, dash, "-2.26"] \arrow[rr, dash, bend right, "-1.70"'] & MnO_4^{=} \arrow[r, dash, "-0.56"] & MnO_4^{-}
\end{tikzcd}$$

For example:

$$2H_2O + Mn^{++} = MnO_2 + 4H^+ + 2\ e; \qquad E^o = -1.23 \text{ volts.}$$

All dissolved substances are at 1 molal concentration.

$$E^\circ = \frac{0.05914}{n} \log K;$$

K = equilibrium constant,
n = number of Faraday's involved.

Copper Sulfate

In the electrolysis of copper sulfate, copper is deposited at the cathode, and oxygen is liberated at the anode.

$$2CuSO_4 + 2H_2O \rightarrow 2Cu + (2H_2SO_4 + O_2) \quad (222).$$

If high current densities are employed (0.02 amp. per square centimeter), a spongelike deposit consisting of metallic copper and cuprous oxide in the ratio of 3:1 is formed at the cathode (124).

In the electrolytic refining of copper, one of the largest of the electrochemical industries, a copper sulfate solution acidified with sulfuric acid is employed. The anode is generally "blister" copper, the impure product of the copper blast furnace (139).

Lead Sulfate

Lead sulfate is sparingly soluble in water and even more insoluble in sulfuric acid solutions. Craig and Vinal (35) have determined the solubility of lead sulfate in sulfuric acid solutions up to 50 percent H_2SO_4.

Because of the very low solubility of lead sulfate in sulfuric acid solutions, lead sulfate solutions are not electrolyzed commercially. However, decomposition of lead sulfate by electrolysis does occur during the charging of lead-acid storage batteries that are used so extensively. These batteries contain an equal number of positive (PbO_2) and negative (Pb) plates in a sulfuric acid electrolyte containing about 30 to 35 percent (by weight) H_2SO_4. The so-called "double-sulfate" theory, first proposed by Gladstone and Tribe in 1882 (71, 72, 73, 74, 75) and now generally accepted as explanation of the reactions in lead-acid batteries, may be stated:

$$PbO_2 + Pb + 2H_2SO_4 \rightleftarrows 2PbSO_4 + 2H_2O.$$

From left to right the equation represents discharge, and from right to left, a charge. The significance of the term "double sulfate" lies in the fact that lead sulfate is formed at both the positive and negative plates during the process of discharge.

A practical approach to normal battery operation is found in the well-known equations for these oxidation-reduction couples (232).

$$\begin{array}{ll} PbO_2 + SO_4^{=} + 4H^+ + 2e = PbSO_4 + 2H_2O; & E^o = +1.685 \text{ volts;} \\ Pb + SO_4^{=} = PbSO_4 + 2e; & E^o = +0.356. \\ \hline PbO_2 + 2SO_4^{=} + 4H^+ + Pb = 2PbSO_4 + 2H_2O; & E^o = +2.041 \text{ volts.} \end{array}$$

The potentials are in volts referred to the hydrogen-hydrogen ion couple as the zero for unit activities and temperature 25° C. Adding the equations gives the reaction for the complete cell and a voltage approximating the observed electromotive force of a commercial cell. The reader is referred to Vinal (232) for an excellent discussion of storage batteries and the theories.

Electrolytic Reduction of Bisulfites (103)

The reduction of bisulfite to hyposulfite by the cathodic reduction of solutions of bisulfite is as follows:

$$2HSO_3^- + 2H^+ + 2e \rightarrow S_2O_4^{=} + 2H_2O.$$

However, the concentration of hyposulfite obtained did not exceed 3 to 4 percent because of the spontaneous decomposition of hyposulfite as follows:

$$2S_2O_4^{=} = S_2O_3^{=} + S_2O_5^{=},$$

a process that is accelerated by the presence of bisulfite ions. Optimum conditions for hyposulfite formation are low temperature, a not too highly acid solution, and a current concentration high enough to avoid prolonged electrolysis.

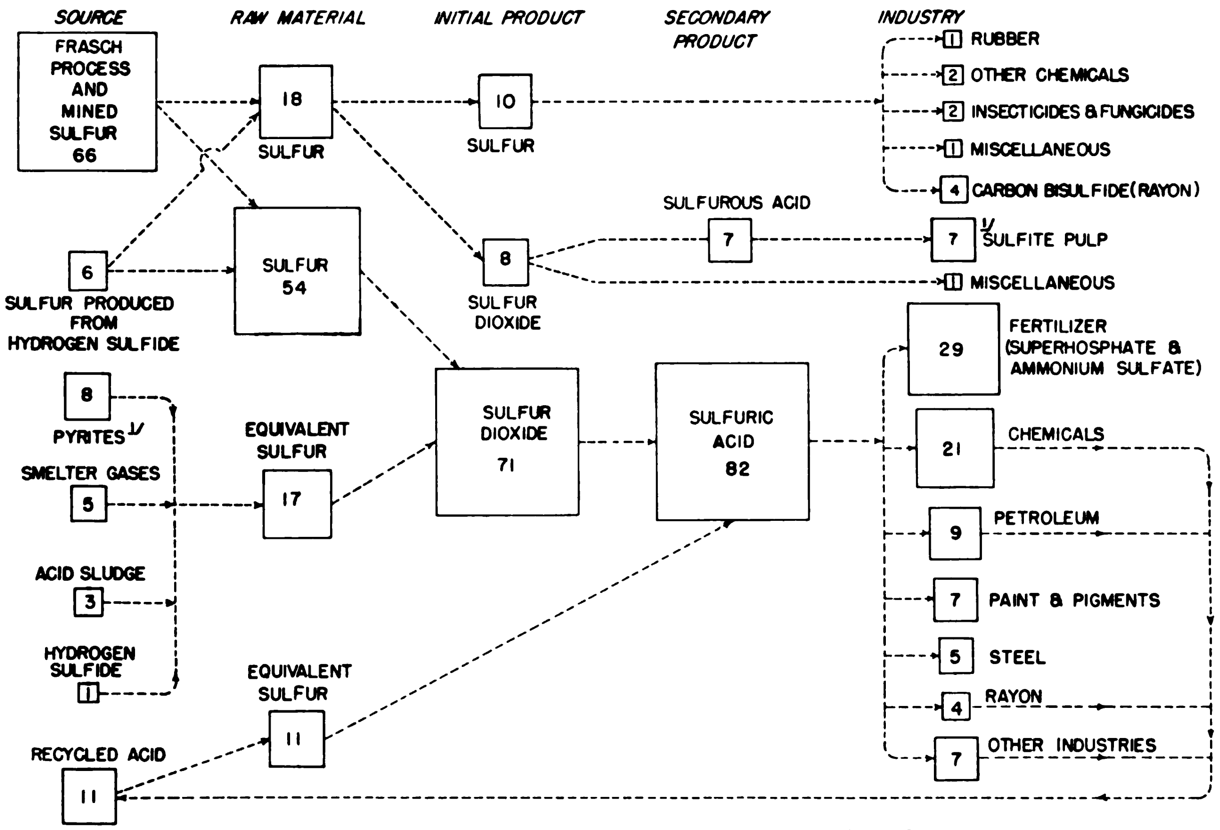
SULFUR - PRODUCTION AND USES

One of the important factors that must be considered in developing any process for removing sulfur dioxide from flue gases is the form in which the sulfur will be recovered as an end product. The ease of storage and handling, the marketability, and the selling price of the product will have considerable influence in determining whether a process is acceptable.

The domestic consumption of sulfur, as related to its source and ultimate use (46), is shown schematically in figure 13. The principal source of sulfur, about two-thirds of the total, in the United States is native sulfur produced from domes by the Frasch process and from surface mines. About 13 percent of the sulfur is available from pyrites and smelter gas, and about 7 percent is recovered in the form of hydrogen sulfide that is obtained in processing sour natural gas or gases derived in coke ovens or petroleum refineries. Other sources of sulfur (14 percent) include recycled sulfuric acid and acid sludge.

Of the total sulfur consumption in 1955 (6,500,000 short tons), 82 percent was in the form of sulfuric acid, 10 percent as elemental sulfur, 7 percent as sulfurous acid, and 1 percent as liquefied sulfur dioxide (46). Demand would thus make sulfuric acid the desired end product, but if there were much disparity between the

Figures Indicate the Percentage of Total Consumption



1/ A small quantity of pyrites is used for sulfite pulp.

BASED ON ESTIMATES BY "CHEMICAL ENGINEERING"

FIGURE 13. - Consumption of Sulfur From all Sources, by Industries in the United States 1952-55 Average. *(Reproduced From Duecker, W.W. and Eddy, E.W. (46).)*

supply and demand the problems of storage, handling, and transporting the acid to a market area could be considerable. In areas of adequate and stable demand for sulfuric acid, acid-producing scrubbing plants might be built. The advantages of elemental sulfur are easier storage on site and lower shipping rates. Sulfur dioxide presents a serious problem of storage and would have to be converted to elemental sulfur or sulfuric acid at the site. Some sulfur dioxide is used in the liquefied form, but this quantity is only about 1 percent of the total sulfur consumed.

Current market prices for sulfur in its principal usable forms are listed in table 2. For comparative purposes, relative values based on a fixed quantity of equivalent sulfur have also been calculated. Ammonium sulfate, which is used principally as a fertilizer, is included, because a scrubbing process proposed by the British employs ammoniacal liquor (36) and ammonium sulfate is the main product.

These data show that, on an equivalent sulfur basis, sulfur and sulfur dioxide would have about the same monetary value; the value of sulfuric acid would be appreciably greater. As ammonium sulfate has a relatively small market compared with other forms of sulfur, only a limited quantity of this material can be produced and sold without seriously lowering its price. Extensive industrial removal of sulfur dioxide would result in tremendous quantities of sulfur products and ultimately might affect the market prices of sulfur in any of its forms. Because of the vast annual consumption and the rising demand in many diversified industries, sulfuric acid and elemental sulfur could be assimilated by the market more readily than the other forms of sulfur.

TABLE 2. - Values of principal forms of sulfur

Form of sulfur	Dollars/ton[1]	Dollars/ton sulfur equivalent
Sulfur (free)	28.00	28.00
Sulfuric acid (100%)	23.50	71.90 (3.06 tons)
Ammonium sulfate	32.00	[2]24.70 (3.94 tons)
Sulfur dioxide (gas)	[3]14.00	28.00 (2 tons)

[1] Chemical and Engineering News (26).

[2] Corrected for ammonia required, allowing $100.00 per ton of ammonia.

[3] Estimated value based on equivalent sulfur in sulfuric acid rather than on current market quotation for liquefied sulfur dioxide.

POSSIBLE METHODS FOR PREVENTING ATMOSPHERIC CONTAMINATION BY SULFUR DIOXIDE

The foregoing survey of the chemistry of sulfur dioxide reveals some avenues of approach that appear more attractive than others in the search for new or improved methods of sulfur dioxide removal from flue gases. The purpose of this section is to present some possibilities that merit further consideration.

The use of fuels that are low in sulfur content would be a considerable aid in decreasing the sulfur dioxide content of the flue gas. Because the supply of such fuels is limited and continuously diminishing, treatment of the fuel before combustion to lower the sulfur content should be considered.

In coal sulfur does not occur as elemental sulfur but is present in organic combination as part of the coal substance and in inorganic combination as pyrite or or marcasite, and, especially in weathered coals, as calcium sulfate. These forms of sulfur are known as organic, pyritic, and sulfate sulfur. In coke, sulfur occurs in organic combination and as sulfides. The great bulk of the commercial coals of the United States contains 1 to 3 percent sulfur.

In the combustion of coal a major part of the sulfur is converted to sulfur dioxide, and only a small quantity (that from the mineral sulfates) remains in the ash. For an average coal containing 1.5 percent sulfur, 3 tons of sulfur dioxide is estimated as produced for every 100 tons of coal burned. Industrial plants burning coal, particularly those using high-sulfur coals, are potential sources of atmospheric pollution. One large power station burning 1 million tons of coal a year would pollute the atmosphere with 30,000 tons of sulfur dioxide. It is estimated that in New York City alone 1,500,000 tons of sulfur dioxide is given off to the atmosphere from the combustion of fuels each year (87).

Reduction of Sulfur in Coal Before Combustion

In the direct reduction of the sulfur content of coal several methods are available: Mechanical cleaning of coal, partial gasification to form a low sulfur char, and complete gasification and a subsequent removal of the sulfur in the form of hydrogen sulfide from the fuel gas.

Mechanical Cleaning of Coal

It has long been recognized that sulfur in organic combinations is a part of the coal substance itself and cannot be removed mechanically. In addition, there is little concentration or segration of organic sulfur in coal immediately adjacent to pyrite deposits, bone coal, shale, or other components of high specific gravity. Nonremovable sulfur, therefore, must be considered as made up almost entirely of organic sulfur and a varying proportion of the total pyritic sulfur. Ordinarily sulfate sulfur, which occurs chiefly as gypsum, may be neglected because it is present in smaller quantities in freshly mined coal than the other two forms of sulfur. The presence of gypsum in important quantities is unusual, but when present its removal is difficult, first, because it occurs in thin plates that tend to adhere to the coal, and second, because its flakiness confers a low falling velocity despite its relatively high specific gravity. The problem of reduction of sulfur by gravitational methods is primarily one of reducing pyritic sulfur. As pyritic sulfur occurs in forms that range in size from microscopic globules to large lenses and balls, its removal depends on its manner of occurrence. The coarser particles of pyrite are easily removable by gravity methods, provided the range of sizes that are treated at one time is not too great (152).

Table 3 (244) illustrates the relationship between the form of sulfur in coal and the reduction of sulfur content obtained in cleaning tests of several coals by using jigs and wet and dry tables. The percentage reduction in total sulfur content obtained is seen to vary inversely with the proportion of the sulfur present in organic form and as fine pyrite locked within the coal. The Pennsylvania coal, containing 30.4 percent of its sulfur in organic and fine pyritic form, allowed a reduction of 63.2 percent in total sulfur content. In contrast, the Indiana coal, containing 76.6 percent of its sulfur in fine pyrite and organic form, allowed a reduction of only 10.7 percent in total sulfur content. The free impurities removed in cleaning the coal from the bottom bench of the Deep River bed, North Carolina, contained less sulfur than occurred in the clean coal; consequently, the sulfur content of this coal was actually increased by cleaning. These examples demonstrate clearly that the form of sulfur in the coal and the degree of its dissemination determine the extent to which it can be removed in cleaning.

TABLE 3. - Reduction in total sulfur and pyritic sulfur obtained in cleaning tests, compared with percentage of fine pyritic and organic sulfur in the raw coal, percent

Coal	Size, inch	Total sulfur in raw coal, percent	Fine pyritic and organic sulfur, percent of total sulfur	Yield of washed coal, percent	Percentage reduction	
					Total sulfur	Pyritic sulfur
Pennsylvania	0-1/4	3.56	30.4	63.0	63.2	81.6
Illinois	3/16-1/4	3.05	56.1	94.1	25.4	45.2
North Carolina[1] ...	0-1/4	1.72	64.7	83.0	21.3	33.4
Do.[1]	0-1	2.92	64.7	83.8	22.4	34.2
Alabama	0-1	2.32	66.3	90.0	21.5	36.0
Indiana	0-1/2	2.32	76.6	84.3	10.7	31.5
North Carolina[2] ...	0-1/4	2.08	86.0	64.5	[3]7.2	[3]1.3

[1] Top bench, Deep River bed.
[2] Bottom bench, Deep River bed.
[3] Concentration of sulfur rather than reduction.

A more recent discussion of the removal of sulfur from coal by methods of coal preparation has been presented (24).

It should be pointed out that, because of the incomplete removal of sulfur, mechanical cleaning of coal could serve only as a preliminary step in removing sulfur.

Coal-cleaning processes in general use gravity-concentration methods. The important processes are grouped according to type in the following classification (134):

Gravity stratification

a. Wet processes
    (1) Jigs
    (2) Launders
    (3) Upward current classifiers
    (4) Heavy mediums
        (a) High density suspensions
        (b) High density solutions
    (5) Tables

b. Dry processes
    (1) Pneumatic tables
    (2) Air jigs
    (3) Air - sand

Methods based upon surface and magnetic properties, and upon electrical conductivity, sliding friction, and strength, although of minor significance, are sometimes employed.

Partial Gasification of Coal

Thermal decomposition of coal by partial gasification will remove part of the sulfur in the form of hydrogen sulfide, which can be removed from the effluent gases and converted to free sulfur.

Low-Temperature Carbonization

Low-temperature carbonization involves the heating of coal from about 900° to 1,200° F. to decompose the coal into several fractions: (1) A semicoke or char, (2) a tar, (3) gases, and (4) water. The char has a reduced sulfur content and high heating value, making it suitable as fuel for industrial purposes (about 30 to 35 percent of the total sulfur is evolved during low-temperature carbonization). The tar is a potential source of chemicals. The gases can be burned as fuel. Sulfur is present in the gas mostly as hydrogen sulfide, which is removed more easily before combustion than sulfur dioxide from flue gas.

The Bureau of Mines has done considerable work in this field (168). A flowsheet of a process developed by the Bureau is shown in figure 14. The coal or lignite is first dried and then carbonized by entrainment with air in an externally heated reactor. Heat is transferred from the wall of the reactor to the suspended mixture, and the air reacts with the coal to supply a substantial part of the heat required for carbonization. All products of reaction, including char, tar vapors, and gas, leave the top of the reactor; the products are then separated in suitable equipment. About one-third of the original sulfur in the lignite is removed from the carbonized

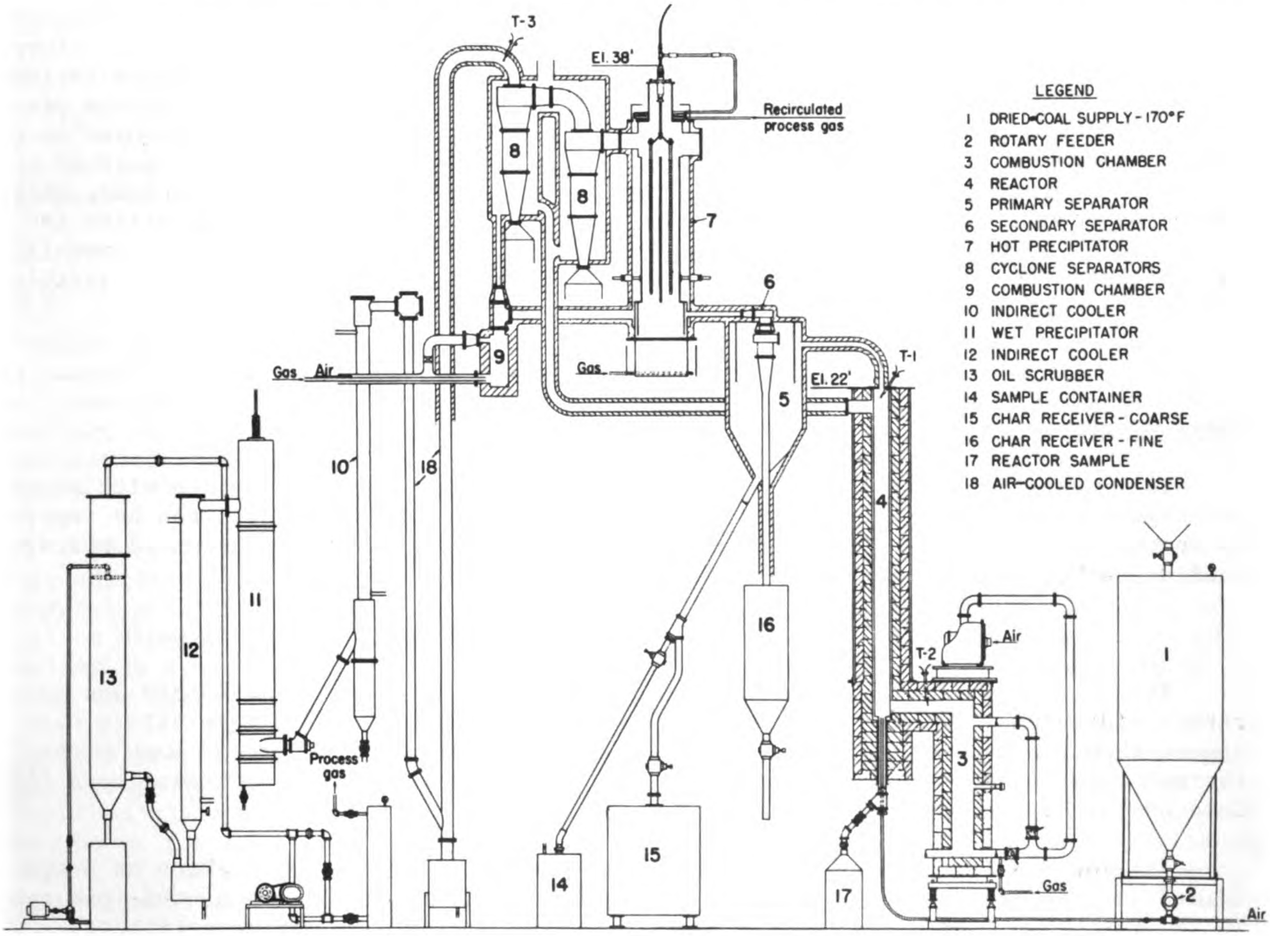


FIGURE 14. - Bureau of Mines Low-Temperature-Carbonization Process. *(Reproduced From Parry, V. F., Landers, W. S., and Wagner, E. O. (168).)*

char. A plant using this process has been constructed by the Texas Power & Light Co. for the Aluminum Company of America at Rockdale, Tex., where a 240,000-kw. steam-electric powerplant will use dried lignite and char to furnish electric power for the aluminum-smelting works.

In addition to the Bureau, several industrial concerns (Pittsburgh Consolidation Coal Company, Olin Mathieson, and Southern Research Institute) are engaged in developing low-temperature carbonization (27).

Carbonization in the Presence of Various Gases

Coal that is heated in a stream of gas is more effectively desulfurized than by thermal decomposition alone. Snow (212) showed that hydrogen was most effective. At 500° C., using 20- to 40-mesh coal, 65 to 70 percent of the sulfur is removed; at 1,000° C., 87 percent is removed. Steam above 500° C. has a marked desulfurizing action, and at 800° C., 84 percent of the sulfur is removed; however, at this temperature the steam-carbon reaction becomes active, and large quantities of the carbon are gasified. The use of inert gases, such as carbon dioxide, nitrogen, or even methane, produces no appreciable increase in desulfurization over that of carbonization in the absence of these gases (212). Desulfurization of coal with steam in a fluidized bed has also been studied (111).

Brewer (18) has shown that the desulfurizing action of ammonia is more effective than that of hydrogen at 800° C. The increased desulfurization of the coal was attributed to the action of nascent hydrogen, which originates from the dissociation of ammonia into hydrogen and nitrogen. The desulfurization is effective in coals of high pyritic sulfur content and in coals containing principally organic sulfur, which cannot be reduced by the usual coal-cleaning methods. The desulfurizing action is increased by adding aluminum oxide, which promotes the decomposition of the ammonia. Carbonization with prior additions of sodium carbonate or lime produces coke further reduced in sulfur content by leaching out the soluble sulfur compounds.

Complete Gasification of Coal

Coal, Oxygen, and Steam

In conversion of a solid fuel to a gaseous fuel through gasification with steam and oxygen, most of the sulfur is converted to hydrogen sulfide, which can be removed by conventional processes. Elemental sulfur can be obtained by oxidation of hydrogen sulfide, as in the modified Claus (68, 86) process.

$$H_2S + 1/2O_2 \rightarrow S + H_2O.$$

The continuous gasification of coal or coke with oxygen instead of air has had rather widespread commercial development in Germany. The use of oxygen allows much higher throughputs; and, since no nitrogen is introduced, a fuel gas of much higher thermal value is obtained. A number of continuous processes have been developed (6). Some of the more important are:

(1) The Winkler process uses a fluidized bed and requires a noncaking or preoxidized coal to prevent agglomeration. This limitation precludes use of this process in the Eastern United States, where virtually all the coal has caking attributes.

(2) The Koppers process, a versatile process that can gasify even caking coals, gasifies pulverized coal in suspension. This more efficient process gasifies 95 percent of the carbon compared with only 55 to 85 percent by the Winkler process.

(3) Lurgi pressure process uses a fixed fuel bed at 20 atmospheres pressure. This process also requires a noncaking coal.

The chief objection to these gasification processes for steam generation is that relatively expensive oxygen must be used, and the thermal efficiency of the overall process is appreciably reduced.

Producer Gas

Producer gas is the least expensive of the manufactured fuel gases. It is made by blowing air or a mixture of air and steam through an incandescent fuel bed. Recent developments (225) using pulverized coal rather than a fixed bed, have greatly increased the output of gas producers of a given size, and with adequate air preheat the producer gas can be obtained at higher temperatures without tar formation. Hot-gas thermal efficiencies of about 95 percent are obtainable. The sulfur in producer gas is mainly hydrogen sulfide and, in smaller quantities, carbon disulfide. The quantity of hydrogen sulfide in producer gas depends on the type of coal, the temperature of the producer, and the air-steam ratio (34). In coals of 0.8 to 2.8 percent sulfur content, 76 to 99 percent of the sulfur is converted to the gaseous form. The hot producer gas may be purified by contacting the gas with alkalized iron oxide to tie up the sulfur as iron sulfide (202). Steam regeneration of the iron sulfide would liberate hydrogen sulfide and allow the sulfur to be recovered as elemental sulfur by suitable processes. The producer gas could be contacted with the iron and iron oxides in a fluidized bed or bed of falling solids. Only a small quantity of the producer gas (1 to 2 percent) would be used to reduce the oxides. The remainder of the gas would be available to generate steam for power. When this method is used, removal of sulfur dioxide from the stack gas would be unnecessary.

Removal of Sulfur Dioxide in the Flue Gas After Combustion

Processes developed for the absorption of sulfur dioxide have been discussed earlier (p. 3.) These processes include the Battersea, the cyclic lime, the basic aluminum sulfate, the sulfidine, and dimethylaniline processes, as well as the use of ammoniacal solutions, sodium sulfite, and magnesium hydroxide. A detailed cost estimate has been completed (54) of the capital and operating costs of the limestone process of Howden-I.C.I. at Fulham, England, and the ammonia and sodium sulfite processes.

Because the cost of removing sulfur dioxide in low concentrations by methods already developed is relatively high, investigation of other methods is recommended. Several promising reactions suggested by the literature search on the chemistry of sulfur dioxide are being investigated by the Bureau. Of importance is recovery of sulfur in a marketable form rather than as a waste product; this would help to defray the cost of removing sulfur dioxide.

In previously developed processes for removing sulfur dioxide from flue gases, absorption in liquids has been used almost exclusively. In these processes the scrubbed gas with some sulfur dioxide remaining is cooled and loses its buoyancy and may hover for some time near ground level, thus partly nullifying the decontaminating effect of the scrubbing process. However, if hot solids are used as the absorbent, the scrubbed gas can be discharged while still hot, allowing the sulfur dioxide content to be rapidly dissipated in the upper atmosphere. With these facts in mind, consideration has been directed toward developing hot absorption processes. Possible processes are:

Solid-phase reactions:

A. Absorption with lime.
B. Absorption with the oxides of manganese.
C. Absorption with lead dioxide.
D. Absorption with cupric oxide.
E. Reaction with a "fouled" Huff catalyst.
F. Adsorption with an impregnated charcoal.

Gas-phase reactions:

A. Catalytic reduction with hydrogen sulfide.
B. Reactions induced photochemically or by electrical discharge.

It is believed that further theoretical studies and bench-scale investigations would provide the additional information required to determine whether these processes can improve the economics of sulfur dioxide removal from flue gases.

Solid-Phase Reactions

Absorption With Lime

Sulfur dioxide may be removed from flue gases by absorption with solid calcium oxide.[13] The sulfur dioxide may be then recovered by thermal dissociation of the calcium sulfite below 1,100° C., followed by the 2-stage Doumani (43) process for a high-purity sulfur, or the calcium sulfite may be directly reduced to free sulfur in the presence of producer gas at 1,200° C.

Absorption of Sulfur Dioxide

Calcium oxide when dry does not absorb an appreciable quantity of sulfur dioxide below 350° C. The addition of water greatly increases its absorptive power. Flue gas entering the absorption tower contains 5 to 8 percent water vapor. The lime would enter at the top of the tower and fall freely while in contact with the ascending gas.

$$CaO + SO_2 \rightleftarrows CaSO_3.$$

Recovery of Sulfur Dioxide

Thermal Dissociation of Calcium Sulfite Followed by Two-Stage Doumani process. - When $CaSO_3$ is heated between 650° and 1,100° C., it decomposes to give sulfur dioxide (60):

$$CaSO_3 \rightleftarrows CaO + SO_2.$$

Below 650° C. it dissociates as follows:

$$4\ CaSO_3 \rightleftarrows CaS + CaSO_4.$$

---

[13] Absorption of SO_2 and SO_3 from flue gases with powdered, < 300-mesh, limestone or lime is the subject of a recent patent (8). The solid absorbent is injected into the flue where the combustion gases are above 360° F.

Digitized by Google Original from THE OHIO STATE UNIVERSITY

The furnaces can be maintained at 900° to 1,100° C.; heat is supplied by the combustion of producer gas. The producer gas can be formed at the site by the steam-air gasification of coal. The sulfur dioxide can then be reduced to a sulfur of high purity by the 2-stage Doumani process as follows:

Stage 1. - Conversion of part of the sulfur dioxide to hydrogen sulfide in a catalyst bed of a gel consisting of iron and aluminum oxides at temperatures above 300° C.

$$SO_2 + 3H_2 \rightarrow 2H_2O + H_2S.$$

Stage 2. - The remainder of the sulfur dioxide is then mixed with the hydrogen sulfide (in a 1:2 ratio) over activated alumina at 100° to 200° C.

$$H_2S + 1/2SO_2 \rightarrow H_2O + 3/2\,S.$$

Direct Reduction of Calcium Sulfite With Producer Gas. - In the presence of a reducing gas such as producer gas, complete conversion to sulfur is possible at 1,200° C. (187).

$$CaSO_3 + CO + H_2 \rightarrow CaO + H_2O + CO_2 + S.$$

In addition to using producer gas as the reducing agent, an additional quantity of producer gas is burned to supply the required heat.

Absorption With Oxides of Manganese

Sulfur dioxide can be removed from flue gases by absorption with manganese dioxide to form manganese sulfate. The manganese dioxide can be recovered by electrolysis or by chemical oxidation of the manganese sulfate. If electrolysis is employed, a dilute solution of sulfuric acid is obtained; if chemical oxidation with ammonium persulfate is used, ammonium sulfate is the byproduct.

Absorption of Sulfur Dioxide

Sulfur dioxide reacts with MnO_2 at flue-gas temperatures to yield manganese sulfate,

$$MnO_2 + SO_2 \rightarrow MnSO_4.$$

Electrolysis of Manganous Sulfate

Electrolysis of manganous sulfate under certain conditions[14] results in the formation of dilute sulfuric acid, together with manganese dioxide at the anode. A variation of this electrolysis is employed commercially in preparing pure zinc. A neutral solution of zinc and manganese sulfates upon electrolysis yields manganese dioxide at the anode and pure zinc at the cathode, and a dilute solution of sulfuric acid is formed (218). The precipitated manganese dioxide could be withdrawn, washed with the incoming fresh water to the electrolytic cell, and returned to the absorption cycle. The water adhering to the oxide will result in a greater rate of absorption and higher capacity. The dilute sulfuric acid could be then concentrated to 78 percent (60° Bé.) acid, employing part of the sensible heat of the flue gas.

---

[14] See p. 49 of this report.

Recovery of Manganese Dioxide by Chemical Oxidation

An active manganese dioxide can be recovered by oxidation of a solution of manganese sulfate with ammonium persulfate according to the following reaction:

$$MnSO_4 + (NH_4)_2S_2O_8 + 4NH_4OH \rightarrow MnO_2 + 3(NH_4)_2SO_4 + 2H_2O.$$

Manganese dioxide precipitates and is filtered off; the filtrate of ammonium sulfate is then electrolyzed to ammonium persulfate:

$$2(NH_4)_2SO_4 + 2H_2O \xrightarrow{\text{electrolysis}} (NH_4)_2S_2O_8 + 2NH_4OH + H_2.$$

Absorption With Lead Dioxide

Absorption of Sulfur Dioxide

A proposed method for removing sulfur dioxide from gas mixtures involves absorption by lead dioxide and subsequent dissociation of the lead sulfate by electrolysis.

The absorption may be expressed by the reaction

$$PbO_2 + SO_2 \rightarrow PbSO_4.$$

It has been found that, at ordinary room temperature, sulfur dioxide reacts with lead dioxide with incandescence forming lead sulfate (91, 192). Lead dioxide is known to be very sensitive to small quantities of sulfur dioxide; lead dioxide has been used in instruments for measuring very small concentrations of sulfur dioxide in the air (184). However, it would be necessary to determine whether or not sulfur dioxide at concentrations of 0.1 to 0.3 volume-percent could be absorbed at rapid enough rate by this oxide.

It is believed that plates constructed and "formed" in a manner similar to those used in lead storage batteries could be used as the absorbent, as the lead dioxide is formed in a porous and spongy mass.

Electrolysis of Lead Sulfate

The dioxide plates, which are partly converted to lead sulfate during the absorption, serve as the anode during electrolysis. Lead, or an inert electrode such as carbon, may serve as the cathode. The electrolytic dissociation of the lead sulfate can occur by one or both of the following reactions:

$$PbSO_4 + 2H_2O \rightarrow PbO_2 + H_2SO_4 + H_2, \qquad (1)$$

$$2PbSO_4 + 2H_2O \rightarrow PbO_2 + Pb + 2H_2SO_4. \qquad (2)$$

The first reaction assumes that the sulfate would be present only on the dioxide plate and not on the plates that serve as the cathode during the electrolysis. If lead plates were used as the cathode and maintained under the electrolyte during the absorption step (to prevent oxidation of the lead to lead oxide by the oxygen present in the flue gas or in the air), some sulfate would also be formed by the chemical action of the sulfuric acid in the electrolyte on the lead plates and hydrogen evolved before the electrolysis. Decomposition would then proceed according to reaction (2), the reaction that occurs during the "charge" of a lead storage battery (232). This latter reaction is the more desirable because the evolution of hydrogen that would occur during electrolysis at the lead dioxide anode, when using an inert cathode in reaction (1) would decrease the efficiency of the electrolysis considerably.

Other important factors that would affect the economics of the process are the rate and degree to which regeneration of the lead sulfate would proceed to the peroxide or lead and the concentration of the acid that would be recovered as product. In respect to the last process, a concentrated acid might be maintained in the process rather than a dilute acid (30 to 35 weight), as required in conventional storage batteries.

Absorption With Cupric Oxide

Sulfur dioxide might be removed from flue gases by absorption with cupric oxide in the presence of oxygen to form cupric sulfate. Sulfur trioxide could then be recovered by thermal dissociation of the cupric sulfate, or the sulfate could be reduced either electrolytically or with hydrogen gas, and sulfuric acid recovered directly. Metallic copper, which would also result from such a reduction, would be oxidized to cupric oxide by the oxygen present in the flue gas.

Absorption of Sulfur Dioxide (in the Presence of Oxygen)

The change in free energy indicates that the reaction,

$$CuO + 1/2O_2 + SO_2 \rightarrow CuSO_4,$$

is thermodynamically possible at flue-gas temperatures (100° to 200° C.). The rate at which this reaction would proceed with concentrations of sulfur dioxide of only 0.1 to 0.3 volume percent would have to be determined experimentally.

Thermal Decomposition of Cupric Sulfate

Thermal decomposition of $CuSO_4$ to CuO and SO_3 in a current of dry air takes place at 736° C. (98).

$$CuSO_4 \xrightarrow{653°\text{-}670°\ C.} \underset{\text{Orange}}{2CuO \cdot SO_3} \xrightarrow{702°\text{-}736°\ C.} \underset{\text{Black}}{CuO + SO_3}.$$

The furnaces could be maintained at this temperature by heat supplied by the combustion of producer gas. The sulfur trioxide could be converted into sulfuric acid by absorption in a sulfuric acid solution; the CuO would be reused in the absorption step.

Electrolytic Reduction of Cupric Sulfate

In the electrolysis of copper sulfate, copper is deposited at the cathode, and oxygen (and sulfuric acid) is liberated at the anode:

$$2CuSO_4 + 2H_2O \rightarrow 2Cu + (2H_2SO_4 + O_2).$$

The proposed process would be similar to electrodeposition practiced in metallurgical engineering (215). This process is, in most respects, the same as the electrolytic refining of copper, except that the anode would be of an inert material and the electrolyte, an acidified solution of cupric sulfate made during absorption. Electrolysis may be conducted in such a manner that copper is deposited as a powder rather than as an adherent plate (45). In this form the copper would be more readily oxidized to cupric oxide with air.

The sulfur dioxide absorbed from a flue gas would thus be a source of production for a dilute sulfuric acid solution, which could be concentrated using the sensible heat of the flue gas.

Reduction of Cupric Sulfate With Hydrogen

Because of the position of copper in the electromotive series, cupric sulfate solutions can be completely reduced with hydrogen, as shown on page 45. Optimum conditions for such a reduction would have to be determined experimentally. Copper would be recovered in powder form for reuse and a dilute sulfuric acid produced.

Reaction With a "Fouled" Huff Catalyst

In a study of catalysts for simultaneous removal of hydrogen sulfide and organic sulfur from Fischer-Tropsch synthesis gas at elevated temperatures by the Bureau of Mines, Morgantown, W. Va. (194), use of a Huff (99) catalyst, composed of the oxides of copper, chromium, and vanadium, was investigated. During this investigation it was discovered that a Huff catalyst that had become "fouled" from scrubbing hydrogen sulfide and organic sulfur was very effective in removing sulfur dioxide. Sulfur dioxide in concentrations of 2 to 1,550 grains per 100 cubic feet of synthesis gas (0.002 to 1.24 volume-percent) was completely removed from the gas. Whether the sulfur dioxide enters into reaction or is physically adsorbed was not explained. On the basis of these tests, use of "fouled" huff catalyst appears to merit further investigation.

Adsorption With an Impregnated Charcoal

Because adsorption of sulfur dioxide on charcoal decreases with increase of temperature, flue-gas temperatures would not be feasible for scrubbing sulfur dioxide with charcoal. However, certain impregnants on activated charcoal are believed to catalytically convert sulfur dioxide to sulfur trioxide in the presence of air. The charcoal would then have greater retentivity for the sulfur trioxide at the higher temperatures. The sulfur trioxide could be recovered under reduced pressure or by steam stripping.

Gas-Phase Reactions

Catalytic Reduction With Hydrogen Sulfide

Catalytic Reaction Over Alumina

A promising method of lowering the sulfur dioxide content in flue gases involves reducing sulfur dioxide with hydrogen sulfide to elemental sulfur. The reaction that occurs readily at atmospheric pressure over a highly purified and specially treated alumina catalyst may be written,

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O.$$

A number of investigators have studied this reaction in the gas phase (43, 129, 211). Whether the reaction between hydrogen sulfide and sulfur dioxide would proceed satisfactorily in a flue gas, when the concentration of sulfur dioxide is considerably lower and where other compounds such as carbon dioxide and oxygen are present, would have to be determined.

To prevent the catalyst from becoming contaminated with sulfur, the temperature in the absorber would have to be maintained above 180° C., probably between 180° and 210° C. At these temperatures the partial pressure of the sulfur product is below the dewpoint (0.91 mm. mercury at 180° C.), and therefore sulfur would not condense on the catalyst. Sulfur would be recovered as a pure liquid from a condenser operated at 120° C. Scrubbed gas would then be discharged relatively hot without loss of buoyancy, as occurs in washing processes where the gas is unavoidably cooled.

Sources of Hydrogen Sulfide

Two potential methods for producing the quantity of hydrogen sulfide required are:

Reaction of Hydrogen With Part of the Sulfur Product to Form H_2S. -

$$H_2 + S \rightarrow H_2S.$$

Reaction of Steam Over Red-Hot Iron Sulfide. -

$$H_2O + FeS \rightarrow H_2S + FeO.$$

The first method is direct and requires only one step; the latter method is indirect, in that the ferrous sulfide must first be formed by reacting sulfur with iron. The iron oxide formed by reaction would be reduced to iron, which would then be converted to ferrous sulfide. In this manner, after the original charge was made, only a small quantity of additional iron would be required as makeup for the losses due to attrition. For the reduction of the iron oxide, a relatively cheap producer gas would seem to be most satisfactory.

Reactions Induced Photochemically or by Electric Discharge

Experimental investigation would be necessary to determine whether sulfur dioxide in dilute concentrations of 0.05 to 0.3 percent could effectively and efficiently be oxidized to sulfur trioxide by the physical methods discussed on pages 41-42. Once formed, the sulfur trioxide could be removed from the effluent gases by electrostatic precipitation and absorption.

CONCLUSIONS

More progress has been made in removing sulfur dioxide from flue gases by gas-washing processes than by other techniques. The developed processes include the Battersea, the Howden-I.C.I. cyclic lime, the basic aluminum sulfate I.C.I., the Lurgi "sulfidine", the Fleming and Fitt dimethylaniline, the ammoniacal liquor, the Johnstone and Singh zinc oxide-sodium sulfite, and the magnesium hydroxide system. A major disadvantage common to all of these wet absorption processes is that cooling of the gases occurs; the scrubbed gas, which still contains some sulfur dioxide, loses its buoyancy and may settle in the immediate vicinity of the plant.

No commercial methods based on adsorption have been developed for removing sulfur dioxide from flue gases. However, the use of an adsorption process is conceivable, and fundamental data for adsorption of sulfur dioxide on carbon, silica gel, platinum, and on the oxides of chromium, iron, and vanadium are presented.

Reduction of sulfur dioxide with gaseous reactants - hydrogen, hydrogen sulfide, carbon monoxide, and methane - occurs at commercially feasible rates and temperatures. Reduction products include sulfur, hydrogen sulfide, and carbon disulfide. Several commercial processes, for example, the Bolidens, Trail, Thiogen, and Asarco, are based on these methods. Reduction of sulfur dioxide with carbon in the form of coke and anthracite has also been practiced on a laboratory and plant scale.

Sulfur dioxide may be oxidized to sulfur trioxide with air or oxygen in the presence of a catalyst as in the contact-acid process, or with ozone, light, or electrical discharge.

Basic metallic oxides in the solid phase might serve as effective absorbents of sulfur dioxide at flue-gas temperatures. Sulfates formed in the absorption could be electrolyzed for recovering sulfur as sulfuric acid and for regenerating metallic oxide. Electrolytic recovery would be desirable at a powerplant installation, where electrical energy is available at a low cost. Thermal decomposition of sulfates could also be employed and sulfur dioxide or sulfur trioxide recovered. Sulfites formed in the absorption also could be thermally decomposed or oxidized with air to the sulfate.

The form in which sulfur is recovered would be an important consideration in developing any process for removing sulfur dioxide from flue gases. Domestic-consumption figures indicate that demand for sulfuric acid would be greater. If a local market is not available, recovery of elemental sulfur may be preferred because it can be stored easily on site and shipped more cheaply than the acid.

Possible methods for preventing atmospheric contamination by sulfur dioxide include those for reducing sulfur in the coal before combustion, and those for removing sulfur dioxide from flue gases after combustion. In the direct reduction of the sulfur content of coal, several methods are available: Mechanical cleaning of coal, partial gasification to form a low-sulfur char, complete gasification, and subsequent removal of the sulfur in the form of hydrogen sulfide from the fuel gas. The Bureau has considered removing sulfur dioxide from flue gases by developing absorption processes, which could be conducted at flue-gas temperatures in order to prevent loss of buoyancy of the flue gases. Several possible methods, including both solid-phase and gas-phase reactions, are suggested as hot-absorption processes.

PHYSICAL PROPERTIES OF SULFUR DIOXIDE

Boiling Point (70)

The boiling point is -10.02° C. at 760 mm. mercury. For temperatures at other pressures see table 4.

Coefficient of Expansion

The coefficient of expansion at constant pressure is

$$\alpha = \frac{1}{V}\left(\frac{\delta V}{\delta T}\right)_P .$$

For a finite difference of temperature the mean coefficient is

$$\alpha_m = \frac{1}{V_1}\left(\frac{V_2-V_1}{t_2-t_1}\right) .$$

Gas (128)

From 0° to 100° C. $\alpha_m = 0.00388$/°C. at 1 atmosphere.

TABLE 4. - Properties of saturated sulfur dioxide (173)

Temp., °F.	Abs. pressure, lb./sq.in.	Volume, cu.ft./lb.		Enthalpy, B.t.u./lb.		Entropy, B.t.u./(lb.)(°R.)	
		Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
t	p	v_f	v_g	h_f	h_g	s_f	s_g
-100	0.294	0.009856	204.7	0	190.1	0	0.5285
- 90	.465	.009954	132.9	3.3	191.4	.0090	.5179
- 80	.710	.010054	89.3	6.5	192.7	.0177	.5081
- 70	1.056	.01015	61.0	9.8	194.0	.0262	.4990
- 60	1.550	.01025	42.6	13.0	195.3	.0344	.4905
- 50	2.225	.01034	30.4	16.3	196.7	.0424	.4827
- 40	3.12	.01044	22.2	19.6	198.0	.0502	.4753
- 30	4.33	.01053	16.4	22.8	199.2	.0579	.4684
- 20	5.88	.01062	12.5	26.0	200.4	.0654	.4620
- 10	7.83	.01072	9.48	29.3	201.7	.0726	.4560
0	10.26	.01082	7.35	32.5	202.8	.0797	.4503
10	13.3	.01092	5.77	35.7	204.0	.0867	.4450
20	16.9	.01103	4.59	39.0	205.3	.0935	.4402
30	21.3	.01114	3.70	42.2	206.4	.1002	.4356
40	26.6	.01125	3.02	45.5	207.7	.1067	.4313
50	32.9	.01137	2.48	48.7	208.7	.1132	.4271
60	40.3	.01149	2.05	52.0	209.8	.1195	.4232
70	49.1	.01162	1.70	55.3	210.8	.1258	.4194
80	59.3	.01175	1.42	58.6	211.7	.1320	.4158
90	71.0	.01189	1.20	61.9	212.6	.1382	.4123
100	84.1	.01204	1.02	65.3	213.5	.1443	.4090
110	99.1	.01219	.868	68.8	214.5	.1503	.4060
120	116.3	.01235	.746	72.2	215.2	.1564	.4030
130	135.8	.01251	.646	75.8	215.8	.1624	.4001
140	157.7	.01269	.554	79.3	216.4	.1684	.3972
150	182	.01288	.481	83.0	217.2	.1744	.3944
160	209	.01309	.418	86.7	217.6	.1805	.3917
170	238	.01330	.364	90.5	218.1	.1865	.3892
180	272	.01350	.319	94.4	218.4	.1926	.3865
190	307	.01371	.281	98.3	218.6	.1988	.3840
200	347	.01396	.246	102.4	218.9	.2050	.3815
210	390	.01422	.217	106.5	218.9	.2112	.3792
220	437	.01453	.191	110.8	218.8	.2175	.3764
230	487	.01487	.168	115.2	218.7	.2239	.3737
240	543	.01527	.147	119.7	217.9	.2304	.3707
250	604	.01574	.129	124.4	216.9	.2370	.3674
260	669	.01628	.113	129.2	215.4	.2438	.3636
270	739	.01690	.0987	134.3	213.3	.2509	.3591
280	816	.01767	.0848	139.7	210.6	.2582	.3543
290	898	.01861	.0723	148.6	203.8	.2703	.3434
300	987	.02002	.0599	152.1	200.7	.2746	.3386
315.4	1143	.03070	.0307	176.2	176.2	.3062	.3062

Liquid (125)

Temperature, °C.	$\frac{V_t}{V_0 \text{°C.}}$	α_m, °C.$^{-1}$	Temperature, °C.	$\frac{V_t}{V_0 \text{°C.}}$	α_m, °C.$^{-1}$
-50	0.9215				0.00206
		0.00156	30	1.0586	
-45	.9287				.00215
		.00157	35	1.0700	
-40	.9360				.00223
		.00158	40	1.0819	
-35	.9434				.00231
		.00160	45	1.0944	
-30	.9510				.00240
		.00162	50	1.1075	
-25	.9587				.00250
		.00164	55	1.1213	
-20	.9666				.00261
		.00166	60	1.1389	
-15	.9746				.00272
		.00169	65	1.1513	
-10	.9828				.00285
		.00172	70	1.1677	
- 5	.9913				.00300
		.00175	75	1.1852	
0	1.0000				.00315
		.00178	80	1.2039	
5	1.0089				.00330
		.00182	85	1.2238	
10	1.0181				.00350
		.00186	90	1.2452	
15	1.0276				.00370
		.00192	95	1.2682	
20	1.0375				.00390
		.00198	100	1.2929	
25	1.0478				

Solid (12)

From -191° to -273° C. $\alpha_m = 0.00025/°$ C.

Critical Constants (174)

Temperature 157.2° C.
Pressure 77.7 atmospheres.
Density 0.52 gm./cm.^{3}

Density

Gas (153)

2.92655 gm./liter at 0° C., 760 mm.
Density as a function of pressure:
Density, gm./liter = a + b P
Density (at 0° C.) = 2.857957 + 0.068593 P

where

P = atmospheres ($\leqq$ 1)
a = limiting density

Original from THE OHIO STATE UNIVERSITY

Liquid and Saturated Vapor (204)

Temperature, °C.	Density of liquid, gm./cm.^{3}	Density of saturated vapor, gm./cm.^{3}	Temperature, °C.	Density of liquid gm./cm.^{3}	Density of saturated vapor, gm./cm.^{3}
-50	1.5590	0.0004	30	1.3574	0.0073
-40	1.5349	.0007	40	1.3296	.0101
-30	1.5106	.0012	50	1.3007	.0140
-20	1.4863	.0020	60	1.2695	.0202
-10	1.4619	.0027	70	1.2360	.0287
0	1.4368	.0029	80	1.1979	.0318
10	1.4113	.0037	90	1.1568	.0479
20	1.3848	.0052	100	1.1119	.0678

Dielectric Constant

The dielectric constant of a medium is defined by ϵ in the equation $F = \frac{Q\,Q'}{\epsilon R^2}$, where F is the force of attraction between two charges Q and Q' separated by distance R in a uniform medium.

Gas (250)

The variation of the dielectric constant with temperature of gaseous sulfur dioxide is shown in the following table at atmospheric pressure ($\nu = 10^6$ cycles per second):

Temperature, °K.	ϵ
265.5	1.010015
267.6	1.009918
295.5	1.008176
297.2	1.008120
366.9	1.005477
443.8	1.003911

These results are represented by the Debye equations

$(\epsilon - 1)\, v\, T = A\, T + B$, where
ϵ is the dielectric constant,
T is the absolute temperature,
v is the specific volume,
$A = 0.001433$,
$B = 2.167$.

Liquid (231)

The variation of the dielectric constant with temperature of liquid sulfur dioxide at atmospheric pressure is shown in the following table ($\nu = 10^6$ cycles per second):

Temperature, °C.	ϵ	Temperature, °C.	ϵ
-16.5	17.27	-42.2	20.27
-19.1	17.43	-44.7	20.80
-21.0	17.73	-47.2	21.10
-22.9	17.93	-52.0	21.73
-25.0	18.17	-54.5	22.10
-27.8	18.46	-55.9	22.26
-30.0	18.73	-57.5	22.57
-32.0	19.00	-60.8	22.93
-35.0	19.27	-63.0	23.33
-40.0	19.99	-65.4	23.73
		-68.8	24.63

Electrical Conductivity (38)

The specific resistivity of liquid sulfur dioxide at temperatures of -30° to -60° C. gave values of 3 to 5 x 10^{-7} ohm^{-1} cm.^{-1}. The temperature dependency is not significant. The presence of traces of water will, however, affect these values.

Enthalpy and Entropy

The engineering thermodynamic properties of enthalpy, entropy, and specific volume for saturated liquid and vapor and superheated vapor are shown in tables 4 and 5. For a more complete tabulation see original reference of Rynning and Hurd (193).

Free Energy of Formation (115)

The free energy of formation of sulfur dioxide from its elements in their reference state at 25° C. is

$$S\ (c,\ rh) + O_2\ (g) = SO_2\ (g),$$

$$\Delta F^\circ_{298.1} = -71{,}750\ \text{cal./mole.}$$

This value can be expressed as a function of temperature as follows:

$$\Delta F^\circ = -70{,}635 + 1.04T \log_{10} T + 2.542 \times 10^{-3}T^2 + \frac{0.084 \times 10^5}{T} - 7.16T.$$

Heat capacity

Gas

The heat capacity at constant pressure is given by the differential

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p .$$

TABLE 5. - Properties of superheated sulfur dioxide (173)

v, volume, cu.ft./lb.; h, enthalpy, B.t.u./lb.; s, entropy, B.t.u./(lb.)(°R.)
Parenthetic figures after pressures are saturation temperatures

Temp., °F.	10 lb./sq.in.abs. (-0.9° F.)			15 lb./sq.in.abs. (15.0° F.)			20 lb./sq.in.abs. (27.0° F.)			30 lb./sq.in.abs. (45.7° F.)			40 lb./sq.in.abs. (59.5° F.)			50 lb./sq.in.abs. (71.1° F.)		
t	v	h	s	v	h	s	v	h	s	v	h	s	v	h	s	v	h	s
0	7.57	202.0	0.4512															
20	7.90	205.9	.4576	5.22	205.4	0.4442												
40	8.24	208.9	.4639	5.45	208.5	.4506	4.06	208.1	0.4409									
60	8.58	211.9	.4699	5.69	211.5	.4567	4.24	211.2	.4472	2.79	210.4	0.4334	2.06	209.7	0.4235			
80	8.93	215.0	.4758	5.92	214.6	.4626	4.41	214.4	.4534	2.91	213.7	.4396	2.15	213.1	.4298	1.70	212.3	0.4217
100	9.27	218.1	.4813	6.15	217.8	.4682	4.59	217.6	.4594	3.03	217.0	.4455	2.25	216.4	.4357	1.78	215.8	.4278
120	9.61	221.2	.4867	6.39	221.0	.4738	4.77	220.7	.4647	3.15	220.2	.4513	2.35	219.6	.4416	1.85	219.0	.4339
140	9.96	224.2	.4919	6.61	224.0	.4791	4.94	223.7	.4700	3.27	223.2	.4568	2.43	222.7	.4471	1.93	222.3	.4396
160	10.29	227.3	.4971	6.84	227.1	.4844	5.11	226.9	.4753	3.38	226.4	.4622	2.52	226.0	.4526	2.00	225.6	.4451
180	10.63	230.5	.5020	7.07	230.3	.4893	5.28	230.1	.4802	3.50	229.6	.4673	2.61	229.2	.4578	2.07	228.8	.4505
200	10.96	233.7	.5070	7.30	233.5	.4942	5.46	233.3	.4851	3.61	232.9	.4722	2.70	232.6	.4630	2.14	232.1	.4558
220	11.30	236.9	.5118	7.53	236.7	.4990	5.63	236.5	.4899	3.73	236.2	.4771	2.78	235.8	.4679	2.21	235.4	.4608
240	11.64	240.1	.5164	7.75	239.9	.5036	5.79	239.7	.4945	3.85	239.4	.4817	2.87	239.2	.4727	2.28	238.7	.4656
260	11.98	243.3	.5209	7.98	243.2	.5081	5.97	242.9	.4991	3.96	242.6	.4863	2.96	242.4	.4773	2.35	242.1	.4703
280	12.32	246.6	.5254	8.20	246.5	.5126	6.13	246.3	.5036	4.07	246.0	.4909	3.04	245.8	.4819	2.42	245.5	.4749
300	12.65	249.9	.5298	8.43	249.7	.5170	6.30	249.6	.5080	4.18	249.3	.4953	3.12	249.1	.4863	2.49	248.9	.4794
320	12.99	253.2	.5342	8.65	253.1	.5214	6.47	253.0	.5124	4.29	252.7	.4997	3.22	252.5	.4907	2.56	252.3	.4838
340	13.33	256.6	.5384	8.87	256.5	.5257	6.64	256.4	.5167	4.41	256.1	.5040	3.30	255.9	.4950	2.63	255.7	.4881
360	13.66	259.9	.5425	9.09	259.8	.5299	6.81	259.7	.5209	4.52	259.5	.5082	3.38	259.3	.4992	2.70	259.1	.4923
380	14.00	263.3	.5466	9.33	263.2	.5340	6.98	263.1	.5250	4.64	262.9	.5123	3.47	262.7	.5033	2.77	262.6	.4964
400	14.35	266.7	.5506	9.55	266.6	.5379	7.15	266.6	.5290	4.75	266.3	.5163	3.56	266.1	.5073	2.83	266.0	.5003
420	14.68	270.1	.5546	9.77	270.1	.5419	7.32	270.0	.5329	4.87	269.8	.5202	3.64	269.6	.5112	2.90	269.5	.5041
440	15.01	273.6	.5585	9.99	273.6	.5458	7.48	273.5	.5368	4.98	273.3	.5241	3.73	273.1	.5151	2.97	273.0	.5081
460	15.35	277.1	.5623	10.21	277.0	.5496	7.65	276.9	.5406	5.09	276.8	.5279	3.81	276.6	.5189	3.04	276.5	.5119
480	15.68	280.6	.5661	10.44	280.5	.5534	7.82	280.4	.5444	5.20	280.3	.5317	3.90	280.2	.5227	3.11	280.0	.5157
500	16.02	284.2	.5697	10.66	284.1	.5571	7.99	284.1	.5481	5.31	283.9	.5354	3.98	283.8	.5264	3.18	283.7	.5194

Temp., °F.	60 lb./sq.in.abs. (80.7° F.)			80 lb./sq.in.abs. (96.9° F.)			100 lb./sq.in.abs. (110.5° F.			150 lb./sq.in.abs. (136.7° F.)			200 lb./sq.in.abs. (156.8° F.)			300 lb./sq.in.abs. (188.0° F.)		
t	v	h	s	v	h	s	v	h	s	v	h	s	v	h	s	v	h	s
100	1.46	215.1	0.4217	1.07	213.9	0.4110												
120	1.53	218.5	.4276	1.13	217.4	.4172	0.882	216.0	0.4088									
140	1.59	221.7	.4334	1.17	220.8	.4232	.924	219.6	.4149	0.587	216.8	0.3993						
160	1.65	225.0	.4391	1.22	224.1	.4290	.966	223.2	.4209	.617	220.7	.4054	0.441	218.1	0.3935			
180	1.71	228.4	.4447	1.27	227.5	.4346	1.004	226.6	.4267	.647	224.4	.4112	.464	222.0	.3998			
200	1.78	231.8	.4501	1.32	230.9	.4400	1.042	230.2	.4323	.677	228.1	.4172	.487	226.0	.4058	0.299	221.3	0.3883
220	1.83	235.1	.4553	1.36	234.3	.4452	1.080	233.6	.4376	.707	231.7	.4227	.509	229.7	.4116	.316	225.5	.3946
240	1.89	238.5	.4603	1.41	237.8	.4502	1.118	237.1	.4427	.735	235.3	.4280	.531	233.5	.4172	.333	229.7	.4005
260	1.95	241.8	.4650	1.45	241.2	.4550	1.154	240.5	.4476	.760	238.9	.4330	.551	237.3	.4226	.348	233.6	.4060
280	2.01	245.2	.4694	1.49	244.7	.4598	1.190	244.1	.4524	.786	242.5	.4379	.571	241.1	.4277	.364	237.8	.4123
300	2.07	248.6	.4736	1.54	248.1	.4643	1.226	247.5	.4570	.810	246.1	.4427	.590	244.8	.4325	.378	241.8	.4174
320	2.12	252.0	.4778	1.59	251.5	.4687	1.263	251.0	.4614	.834	249.8	.4473	.610	248.5	.4372	.392	246.0	.4223
340	2.18	255.5	.4820	1.63	255.1	.4731	1.298	254.6	.4656	.858	253.4	.4517	.629	252.2	.4418	.405	249.8	.4270
360	2.24	258.9	.4862	1.67	258.5	.4773	1.333	258.1	.4697	.882	257.0	.4561	.652	255.8	.4462	.419	253.5	.4316
380	2.30	262.4	.4903	1.71	262.0	.4814	1.367	261.6	.4737	.905	260.5	.4603	.667	259.4	.4505	.433	257.2	.4360
400	2.36	265.9	.4943	1.76	265.5	.4854	1.403	265.1	.4777	.929	264.1	.4645	.685	263.1	.4548	.446	261.0	.4404
420	2.41	269.4	.4983	1.80	269.0	.4893	1.439	268.6	.4817	.952	267.6	.4686	.704	266.7	.4589	.458	264.7	.4447
440	2.47	272.9	.5023	1.85	272.5	.4932	1.474	272.1	.4857	.974	271.2	.4726	.727	270.3	.4630	.471	268.4	.4489
460	2.53	276.4	.5061	1.89	276.0	.4970	1.509	275.7	.4896	.996	274.8	.4766	.740	273.9	.4670	.484	272.1	.4531
480	2.59	279.9	.5099	1.93	279.5	.5008	1.543	279.2	.4935	1.018	278.4	.4805	.759	277.6	.4710	.497	275.9	.4572
500	2.64	283.5	.5136	1.97	283.1	.5045	1.578	282.8	.4973	1.039	282.1	.4843	.776	281.3	.4748	.509	279.7	.4611

Temp., °F.	400 lb./sq.in.abs. (212.0° F.)			500 lb./sq.in.abs. (232.5° F.)			600 lb./sq.in.abs. (249.5° F.)			800 lb./sq.in.abs. (278.0° F.)			1000 lb./sq.in.abs. (301.5° F.)		
t	v	h	s	v	h	s	v	h	s	v	h	s	v	h	s
220	0.216	221.1	0.3810												
240	.232	225.6	.3875	0.168	220.2	0.3753									
260	.246	230.0	.3936	.182	225.2	.3820	0.138	220.4	0.3714						
280	.255	234.4	.3994	.195	230.2	.3883	.150	226.3	.3783	0.0914	212.5	0.3560			
300	.269	238.8	.4049	.206	235.0	.3944	.162	231.4	.3849	.1035	221.8	.3649			
320	.282	243.1	.4102	.216	239.7	.4002	.172	236.5	.3913	.1140	229.1	.3734	0.0761	217.3	0.3504
340	.293	247.2	.4154	.226	244.2	.4059	.181	241.2	.3976	.1230	234.9	.3814	.0865	226.1	.3655
360	.305	251.0	.4203	.236	248.5	.4114	.189	245.8	.4035	.1308	240.0	.3887	.0944	232.7	.3760
380	.315	254.8	.4251	.244	252.6	.4165	.197	250.1	.4090	.1379	244.8	.3951	.1014	238.6	.3821
400	.325	258.8	.4298	.253	256.7	.4212	.205	254.4	.4138	.1446	249.5	.4004	.1076	244.2	.3888
420	.335	262.6	.4343	.261	260.6	.4257	.212	258.5	.4184	.1510	254.0	.4056	.1135	249.1	.3941
440	.346	266.4	.4386	.270	264.6	.4301	.220	262.5	.4229	.1572	258.3	.4106	.1190	253.9	.3998
460	.356	270.2	.4428	.279	268.5	.4345	.227	266.4	.4273	.1632	262.5	.4153	.1243	258.4	.4051
480	.366	274.1	.4469	.287	272.4	.4387	.234	270.5	.4317	.1691	266.8	.4200	.1296	262.8	.4101
500	.376	278.0	.4509	.295	276.3	.4428	.241	274.6	.4359	.1746	271.0	.4245	.1345	267.1	.4147

The following values have been calculated by Kelley (115) by adding the vibrational heat capacity to the classical value for the translational and rotational heat capacities:

Temperature, °K.	Cp(cal./deg. mole)	Temperature, °K.	Cp(cal./deg. mole)
298.1	9.52	1,300	13.26
400	10.37	1,400	13.34
500	11.08	1,500	13.43
600	11.68	1,600	13.47
700	12.10	1,700	13.52
800	12.43	1,800	13.56
900	12.69	1,900	13.59
1,000	12.89	2,000	13.62
1,100	13.04	2,500	13.72
1,200	13.17	3,000	13.78

The foregoing heat capacities may be represented by the equation,

$$Cp = 11.40 + 1.414x10^{-3}T - 2.045x10^{5}T^{-2},$$

which fits with an average deviation of 0.15 unit for the range 298.1° to 1,500° K., and an average deviation of 0.20 unit for the range 298.1° to 2,000° K.

For the variation of Cp with pressure, see Fiske (56).

The heat capacity at constant volume is given by the differential

$$C\ v = \left(\frac{\partial\ H}{\partial\ T}\right)_v .$$

The following table is reported in Gmelin (84).

Temperature, °C.	Cv (cal./deg. mole)
0	7.2
100	8.1
200	9.2
500	9.8
1,200	10.6
2,000	11.1

Heat-Capacity Ratio

$$\frac{Cp}{Cv} = \gamma .$$

As a function of temperature (66),

Temperature, °C.	(Cp/Cv) real	(Cp/Cv) ideal
12-13	1.2742	1.2811
143.0	1.2599	1.3015
234.7	1.2452	1.2981
313.4	1.2397	1.2965
325.4	1.2356	1.2722
394.7	1.2223	1.2753
489.5	1.2130	1.2535

As a function of pressure (28) at 25.1° C.,

Pressure, atm.	γ
0	1.2638
0.9970	1.2825
2.241	1.3135
2.8705	1.3329
3.641	1.3561

Liquid (70)

Temperature, °C.	Cp (cal./deg. mole)	Temperature, °C.	Cp (cal./deg. mole)
-71.36	20.97	-33.01	20.79
-65.84	20.95	-27.88	20.71
-60.50	20.91	-22.59	20.72
-55.28	20.90	-17.38	20.69
-50.13	20.85	-12.24	20.69
-44.05	20.83	-10.02	Boiling point
-38.01	20.79		

Solid (70)

Temperature, °C.	Cp (cal./deg. mole)	Temperature, °C.	Cp (cal./deg. mole)
-257.90	0.860	-174.80	11.36
-255.78	1.155	-169.28	11.68
-253.37	1.621	-163.60	11.98
-250.51	2.211	-158.36	12.21
-247.43	2.864	-152.73	12.42
-244.14	3.570	-148.54	12.55
-240.66	4.311	-142.74	12.87
-238.23	4.821	-137.27	13.15
-233.85	5.672	-132.18	13.32
-229.81	6.325	-126.91	13.63
-225.94	6.930	-121.38	13.94
-221.82	7.535	-116.12	14.15
-217.35	8.106	-111.07	14.46
-212.25	8.727	-105.81	14.69
-206.76	9.252	-100.43	14.92
-201.42	9.687	- 95.26	15.25
-196.12	10.11	- 90.28	15.64
-190.02	10.54	- 84.87	15.93
-184.26	10.86	- 80.28	16.16
-180.00	11.05	- 75.46	Melting point

Heat of Formation

The standard heat of formation of sulfur dioxide from its elements in their reference state at 25° C. is

$$S\ (c,\ rh) + O_2\ (g) = SO_2\ (g),$$

$$\Delta H^\circ_{298.16} = -70{,}940 \pm 50\ \text{cal./mole}\ (\underline{47}).$$

The variation of ΔH with temperature is given by

$$\Delta H = 70635 - 0.45T - 2.542\text{x}10^{-3}T^2 + \frac{0.168\text{x}10^{-5}}{T} \quad (115).$$

The heat of formation of aqueous solutions is as follows (191):

$$S\ (c,\ rh) + O_2\ (g) = SO_2\ (aq.),$$

	Moles H_2O	$\Delta H°$, kcal./mole.
SO_2 in	200	-78.5
	300	-78.60
	400	-78.74
	500	-78.85
	1,000	-79.27
	2,000	-79.74
	3,000	-80.05
	4,000	-80.26
	5,000	-80.41
	10,000	-80.86

Heat of Fusion (70)

$$SO_2\ (s) = SO_2\ (l),$$

ΔH_m = 1,769 ± 2 cal./mole (at -75.46° C.).

Heat of Vaporization

The latent heat of vaporization at 760 mm. pressure (70)

$$SO_2\ (l) = SO_2\ (g),$$

ΔH_L = 5,960 ± 4 cal./mole (at -10.02° C.).

At other temperatures the following smoothed values were obtained by Perlick (171):

Temperature, °C.	ΔH_L, cal./gram	Temperature, °C.	ΔH_L, cal./gram
-20	98.1	10	91.0
-10	96.0	20	88.2
0	93.6	30	85.2

Magnetic Susceptibility (169)

X = specific susceptibility, units = C.G.S. electromagnetic units.

The values are positive for paramagnetic bodies; negative for diamagnetic.

$X_{\text{liquid } SO_2}$ at 16° C. (referred to water = $-0.75\text{x}10^{-6}$) = $-0.297\text{x}10^{-6}$.

Molecular Weight

64.066 (238).

Melting Point (70)

-75.46° C. at triple point.

Refractivity

Refractivity = n-1, where n is the index of refraction.

Specific refractivity = $\frac{n-1}{d}$, where d is the density.

Molecular refractivity = (specific refractivity) (molecular weight).

Index of refraction = $\frac{\text{velocity of light in vacuum}}{\text{velocity of light in substance}}$.

The index of refraction varies with the wavelength of the light.

Gas (100)

$(n-1)_o$ = refractivity at infinite dilution and 0° C.

λ in Å	$(n-1)_o \times 10^7$	λ in Å	$(n-1)_o \times 10^7$
4,047.70	6,843.3	5,087.23	6,661.6
4,359.56	6,773.8	5,462.25	6,627.1
4,679.46	6,718.3	5,771.20	6,601.3
4,801.25	6,699.2	5,792.26	6,599.4

The dispersion formula corresponding to these data is

$$(n-1)_o = \frac{5.220 \times 10^{27}}{8178 \times 10^{27} - \nu^2}; \nu = \text{frequency.}$$

Liquid (13)

Sodium light at 15° C. n = 1.350.

Solubility in Water (201)

(This reference is fairly early work but is still being extensively quoted.)

Temperature, °C.	I	q	Temperature, °C.	I	q
0	79.789	22.83	17	43.939	12.59
1	77.210	22.09	18	42.360	12.14
2	74.691	21.37	19	40.838	11.70
3	72.230	20.66	20	39.374	11.28
4	69.828	19.98	21	37.970	10.88
5	67.485	19.31	22	36.617	10.50
6	65.200	18.65	23	35.302	10.12
7	62.973	18.02	24	34.026	9.76
8	60.805	17.40	25	32.786	9.41
9	58.697	16.80	26	31.584	9.06
10	56.647	16.21	27	30.422	8.73
11	54.655	15.64	28	29.314	8.42
12	52.723	15.09	29	28.210	8.10
13	50.849	14.56	30	27.161	7.80
14	49.033	14.04	35	22.489	6.47
15	47.276	13.54	40	18.766	5.41
16	45.578	13.05			

Where I = volume of gas in cc., dissolved by 1 volume of water at total pressure of 760 mm. (partial pressure of gas plus aqueous tension at the stated temperature);

q = weight of gas in grams dissolved in 100 grams water at total pressure of 760 mm. (partial pressure of gas plus aqueous tension at the stated temperature).

Critical literature survey and correlation were made on the system sulfur dioxide-water (175).

Specific Gravity (125)

The specific gravity of liquid sulfur dioxide in the range of -50° to + 100° C.

Temperature, °C.	Specific gravity	Temperature, °C.	Specific gravity
-50	1.5572	25	1.3695
-45	1.5452	30	1.3556
-40	1.5331	35	1.3411
-35	1.5211	40	1.3264
-30	1.5090	45	1.3111
-25	1.4968	50	1.2957
-20	1.4846	55	1.2797
-15	1.4724	60	1.2633
-10	1.4601	65	1.2464
- 5	1.4476	70	1.2289
0	1.4350	75	1.2108
+ 5	1.4223	80	1.1920
10	1.4095	85	1.1726
15	1.3964	90	1.1524
20	1.3831	95	1.1315
		100	1.1100

Surface Tension (204)

The surface tension of liquid sulfur dioxide is reported as follows:

Temperature, °C.	Surface tension, dynes/cm.	Molecular surface energy, ergs	Temperature, °C.	Surface tension, dynes/cm.	Molecular surface energy, ergs
-50	34.48	410	30	20.30	265
-40	32.69	393	40	18.23	241
-30	30.91	376	50	16.43	219
-20	29.33	361	60	14.73	199
-10	27.73	344	70	12.86	179
0	25.83	324	80	11.03	155
+10	24.05	305	90	9.33	133
20	22.19	285	100	7.60	110

Thermal Conductivity

Gas

Temperature dependency (42)

$$k_{0^\circ C.} = 206 \times 10^{-7} \text{ cal./cm. sec. °C.}$$

$$k_{18.89^\circ C.} = 221.6 \times 10^{-7} \text{ cal./cm. sec. °C.}$$

Temperature coefficient between 0° and 20° C. $\beta = 0.0039/°C$.

Pressure dependency (61)

k measured at several temperatures between 2.5° and 22.0° C. and pressures between 3 and 800 mm.

$$k_{3.4° C.} = 2.097\ (1 + 0.0232\ P)\ 10^{-5}\ \text{cal./cm. sec. °C.;}$$
$$k_{22° C.} = 2.295\ (1 + 0.0145\ P)\ 10^{-5}\ \text{cal./cm. sec. °C.,}$$

where P = atmospheres.

Liquid

Kardos (122) measured the thermal conductivity of liquid sulfur dioxide at 5.25 atmospheres between -13° C. and 25° C.

Temperature	kx10^5, cal./cm. sec. °C.
-12.73	52.68
- 3.75	50.36
+ 6.50	49.91
+15.75	48.41
+24.70	46.58

The thermal conductivity of liquid sulfur dioxide between -13° and +25° C. may be expressed by

$$k = 0.0005050\ (1-0.00296\ t),$$

where t = °C.

Thermodynamic Functions (49)

The thermodynamic functions and properties, such as free-energy function, heat-content function, entropy, heat content, and heat capacity have been calculated, assuming a rigid rotator and harmonic oscillator for sulfur dioxide in the ideal gas state of unit pressure.

Temp., °K.	Free-energy function, $\frac{F°-H_0°}{T}$	Heat-content function, $\frac{H°-H_0°}{T}$	Entropy, S°	Heat capacity, $C_p°$	Heat content, $H°-H_0°$
	Cal./deg. mole				Cal./mole
298.16	-50.84	8.45	59.29	9.53	2,519
300	-50.89	8.46	59.35	9.54	2,538
400	-53.38	8.84	62.22	10.39	3,536
500	-55.40	9.22	64.62	11.12	4,610
600	-57.11	9.60	66.71	11.71	5,760
700	-58.61	9.94	68.55	12.17	6,958
800	-59.96	10.24	70.20	12.53	8,192
900	-61.18	10.51	71.69	12.82	9,459
1,000	-62.30	10.75	73.05	13.03	10,750
1,100	-63.34	10.97	74.31	13.20	12,067
1,200	-64.30	11.16	75.46	13.35	13,392
1,300	-65.20	11.34	76.54	13.47	14,742
1,400	-66.04	11.50	77.54	13.57	16,100
1,500	-66.84	11.64	78.48	13.65	17,460

Vapor Pressure

The vapor pressure of liquid sulfur dioxide from -75° to -10° C. (70):

Temperature, °C.	Pressure, mm. Hg.	Temperature, °C.	Pressure, mm. Hg.
-75.46	[1]12.56	-44.810	121.57
-72.297	16.52	-39.978	163.11
-67.958	23.58	-34.990	217.62
-63.519	33.40	-29.516	293.80
-59.008	46.77	-23.463	402.27
-54.498	64.37	-16.725	558.97
-49.923	87.55	- 9.615	773.82

---

[1] Triple-point pressure.

The vapor pressure of liquid sulfur dioxide from 0° to the critical pressure (22):

Temperature, °C.	Pressure, atm.	Temperature, °C.	Pressure, atm.
0	1.53	101.54	28.31
8.30	2.07	110.67	33.63
10.15	2.32	120.35	40.68
21.65	3.37	131.94	50.18
32.40	4.92	144.20	61.93
41.90	6.70	145.55	63.28
50.40	8.49	151.15	69.67
64.68	12.49	156.11	75.88
80.17	17.67	156.30	75.93
90.56	22.32	157.50	77.79

Vapor Pressure of Aqueous Solutions (101)

The partial pressures of sulfur dioxide and water over aqueous solutions of sulfur dioxide are shown on table 6.

Viscosity

The C.G.S. unit for absolute viscosity is the poise

$$1 \text{ poise} = 1\ \frac{(\text{dyne})\ (\text{sec.})}{\text{cm.}^2} = 1\ \frac{\text{gram}}{(\text{sec.})\ (\text{cm.})}.$$

$$1 \text{ centipoise} = 0.01 \text{ poise}.$$

To convert centipoises into English engineering units

$$(\text{Centipoise})\ (0.000672) = \frac{\text{lb. mass}}{(\text{ft.})\ (\text{sec.})} = \frac{(\text{poundal})\ (\text{sec.})}{\text{ft.}^2},$$

$$(\text{Centipoise})\ (2.42) = \frac{\text{lb. mass}}{(\text{ft.})\ (\text{hr.})}.$$

Stakelbeck (214) measured the absolute viscosity of sulfur dioxide, liquid and gaseous, from 0.5 to 8 atmospheres and from -20° to 40° C. by means of Lawaczek dropping method. The values are tabulated below. (The original data were converted from the units of $\frac{\text{Kg-sec.}}{\text{m.}^2}$ to centipoises.)

TABLE 6. - Partial pressures of water and sulfur dioxide over aqueous solutions of sulfur dioxide

Partial pressures of H_2O and SO_2, mm. Hg.

SO_2 per 100 gram water, grams	10° C.		20° C.		30° C.		40° C.		50° C.		60° C.		70° C.		80° C.		90° C.		100° C.		110° C.		120° C.		130° C.	
	H_2O	SO_2	H_2O	SO_2	H_2O	SO_2	H_2O	SO_2	H_2O	SO_2	H_2O	SO_2	H_2O	SO_2	H_2O	SO_2	H_2O	SO_2	H_2O	SO_2	H_2O	SO_2	H_2O	SO_2	H_2O	SO_2
0.0	9.2	-	17.5	-	31.8	-	55.3	-	92.5	-	149.5	-	234	-	355	-	526	-	760	-	1,074	-	1,488	-	2,026	-
0.5	9.2	21	17.5	29	31.7	42	55.2	60	92.3	83	149.2	111	234	144	354	182	525	225	758	274	1,072	326	1,486	377	2,024	420
1.0	9.2	42	17.4	59	31.7	85	55.1	120	92.2	164	149.0	217	233	281	354	356	524	445	757	548	1,071	661	1,484	775	2,022	879
1.5	9.2	64	17.4	90	31.6	129	55.0	181	92.0	247	148.8	328	233	426	353	543	523	684	756	850	1,070	1,032				
2.0	9.1	86	17.4	123	31.6	176	55.0	245	91.9	333	148.6	444	233	581	353	746	523	940								
2.5	9.1	108	17.4	157	31.5	224	54.9	311	91.8	421	148.3	562	232	739	352	956										
3.0	9.1	130	17.3	191	31.5	273	54.7	378	91.6	511	148.1	682	232	897												
3.5	9.1	153	17.3	227	31.5	324	54.7	447	91.5	603	147.9	804														
4.0	9.1	176	17.3	264	31.4	376	54.6	518	91.4	698																
4.5	9.1	199	17.3	300	31.4	428	54.5	588	91.2	793																
5.0	9.1	223	17.2	338	31.3	482	54.4	661																		
5.5	9.0	247	17.2	375	31.3	536	54.4	733																		
6.0	9.0	271	17.2	411	31.2	588	54.3	804																		
6.5	9.0	295	17.2	448	31.2	642																				
7.0	9.0	320	17.1	486	31.1	698																				
7.5	9.0	345	17.1	524	31.1	752																				
8.0	9.0	370	17.1	562	31.0	806																				
8.5	9.0	395	17.0	600																						
9.0	9.0	421	17.0	638																						
9.5	8.9	447	17.0	676																						
10.0	8.9	473	17.0	714																						
10.5	8.9	499	17.0	751																						
11.0	8.9	526	16.9	789																						
11.5	8.9	553																								
12.0	8.9	580																								
12.5	8.9	608																								
13.0	8.8	635																								
13.5	8.8	662																								
14.0	8.8	689																								
14.5	8.8	716																								
15.0	8.8	743																								
15.5	8.8	771																								
16.0	8.8	799																								

Original from THE OHIO STATE UNIVERSITY

Viscosity μ (10^2), centipoises

Temp., °C.	Pressure, atm.							
	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
-20	1.05	49.03	49.62	50.21	50.63	51.00	51.29	51.53
-10	1.09	1.12	44.33	44.96	45.43	45.90	46.29	46.63
0	1.13	1.17	1.22	39.23	39.79	40.26	40.65	41.02
10	1.19	1.22	1.26	1.30	33.29	33.81	34.27	34.67
20	1.24	1.26	1.28	1.33	1.38	1.45	27.40	27.85
30	1.29	1.30	1.31	1.33	1.35	1.39	1.44	1.52
40	1.36	1.37	1.38	1.40	1.42	1.44	1.47	1.51

Temp., °C.	Pressure, atm.							
	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0
-20	51.80	52.00	52.17	52.32	52.45	52.58	52.70	52.81
-10	46.94	47.22	47.47	47.71	47.91	48.10	48.30	48.48
0	41.32	41.61	41.88	42.09	42.30	42.48	42.66	42.81
10	35.03	35.30	35.58	35.79	36.01	36.19	36.34	36.53
20	28.29	28.68	28.98	29.30	29.54	29.78	30.01	30.20
30	1.63	-	-	-	-	-	-	-
40	1.56	1.62	1.69	1.77	-	-	-	-

The following values were obtained for the saturated vapor and liquid (214):

Temperature, °C.	Pressure, atm.	Liquid, (10^2) centipoises	Vapor (10^2) centipoises
-20	0.648	48.54	1.06
-10	1.033	43.69	1.13
0	1.580	38.49	1.23
+10	2.34	33.10	1.35
+20	3.35	27.26	1.51
+30	4.67	-	1.69
+40	6.35	-	1.83

A nomograph of the viscosities of gaseous and liquid sulfur dioxide is given by Genereaux (69).

ABBREVIATIONS OF JOURNAL REFERENCES

Abbreviations	Journal titles
Am. Gas Assoc., Proc.	American Gas Association, Proceedings.
Ann. Chem., Justus Liebigs	Annalen der Chemie, Justus Liebigs.
Ann. chim. phys.	Annales de chimie et de physique.
Ann. phys.	Annales de physique.
Ann. Physik	Annalen der Physik.
Ber. deut. chem. Gesell.	Berichte der deutschen chemischen Gesellschaft.
Bull. Am. Inst. Min. Met. Eng.	Bulletin of the American Institute of Mining and Metallurgical Engineers.
Bull. soc. chim. Belg.	Bulletin de la société chimique de Belgique.
Bureau of Mines Bull.	Bureau of Mines Bulletin (United States).
Bureau of Mines Rept. of Investigations	Bureau of Mines Report of Investigations (United States).
Canadian Chem. Process Ind.	Canadian Chemistry and Process Industries (now Canadian Chemical Processing).
Canadian Jour. Phys.	Canadian Journal of Physics.
Canadian Jour. Res.	Canadian Journal of Research.
Chem. Abs.	Chemical Abstracts.
Chem. Eng. News	Chemical and Engineering News.
Chem. & Ind.	Chemistry & Industry.
Chem. Met. Eng.	Chemical and Metallurgical Engineering (now Chemical Engineering).
Chem. Eng.	Chemical Engineering.
Chem. Eng. Progress	Chemical Engineering Progress.
Chem. Rev.	Chemical Reviews.
Chem.-Ztg.	Chemiker-Zeitung.
Combustion	Combustion.
Compt. rend.	Comptes rendus hebdomadaires des séances de l'académie des sciences.
Eng. Min. Jour.	Engineering and Mining Journal.
Engineering	Engineering.
Gazz. chim. ital.	Gazzetta chimica italiana.
Giorn. chim. ind. applicata	Giornale di chimica industriale ed applicata.
Glückauf	Glückauf.
Helv. Chim. Acta	Helvetica Chimica Acta.
Ind. Chemist	Industrial Chemist and Chemical Manufacturer.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
Ind. Eng. Chem., news ed.	Industrial and Engineering Chemistry, news edition.
Iva	Iva.
Jour. Am. Chem. Soc.	Journal of the American Chemical Society.
Jour. Chem. Ed.	Journal of Chemical Education.
Jour. Chem. Ind. (U.S.S.R.)	Zhurnal Khimicheskoĭ Promyshlennosti, U.S.S.R. (Journal of Chemical Industry).
Jour. Chem. Phys.	Journal of Chemical Physics.
Jour. Chem. Soc.	Journal of the Chemical Society (London).
Jour. chim. phys.	Journal de chimie physique.
Jour. Gen. Chem. (U.S.S.R.)	Zhurnal Obshcheĭ Khimii, U.S.S.R. (Journal of General Chemistry).
Jour. Indian Chem. Soc.	Journal of the Indian Chemical Society.
Jour. Inst. Fuel	Journal of the Institue of Fuel.
Jour. Iron and Steel Inst.	Journal of the Iron and Steel Institute, (London).
Jour. Metals	Journal of Metals.
Jour. Phys. Chem.	Journal of Physical Chemistry.

Abbreviations	Journal titles
Jour. Phys. Chem. (U.S.S.R.)	Zhurnal Fizicheskoĭ Khimii, U.S.S.R. (Journal of Physical Chemistry).
Jour. prakt. Chem.	Journal für praktische Chemie.
Jour. Soc. Chem. Ind.	Journal of the Society of Chemical Industry (London).
Jour. Soc. Chem. Ind. (Proc.)	Journal of the Society of Chemical Industry (Proceedings).
Kolloid-Ztschr.	Kolloid-Zeitschrift.
Korrosion u. Metallschutz	Korrosion und Metallschutz unter Einbeziehung des allgemeinen Werkstoffschutzes.
Met. Chem. Eng.	Metallurgical and Chemical Engineering (now Chemical Engineering).
Metallges., Periodic Rev.	Metallgesellschaft, Periodic Review.
Metallurgie	Metallurgie.
Metals Technol.	Metals Technology (now Journal of Metals).
Min. Cong. Jour.	Mining Congress Journal.
Min. Eng.	Mining Engineering.
Nat. Bureau of Standards, Res. Jour.	National Bureau of Standards, Research Journal.
Nat. Bureau of Standards, Sci. Papers	National Bureau of Standards, Scientific Papers.
Nature	Nature (London).
Oil Gas Jour.	Oil and Gas Journal.
Phys. Rev.	The Physical Review.
Proc. Roy. Soc. (London)	Proceedings of the Royal Society (London).
Przemysl Chem.	Przemysl Chemiczny (Chemical Industry).
Pulp & Paper Mag. Canada	Pulp & Paper Magazine of Canada.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas.
Refrig. Eng.	Refrigerating Engineering.
Rev. quím. ind.	Revista de química industrial. (Rio de Janeiro.)
Roczniki Chem.	Roczniki Chimii.
Soc. Chem. Ind. (London) Chem. Eng. Group Proc.	Society of Chemical Industry (London) Chemical Engineering Group, Proceedings.
TAPPI	Technical Association of the Pulp and Paper Industry.
Trans. AICE	Transactions, American Institute of Chemical Engineers.
Trans. ASME	Transactions, American Society of Mechanical Engineers.
Trans. AIME	Transactions, American Institute of Mining and Metallurgical Engineers.
Trans. Electrochem. Soc.	Transactions of the Electrochemical Society, Inc.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Roy. Soc. (London)	Transactions of the Royal Society (London), Philosophical.
Univ. Illinois, Eng. Exper. Sta. Bull.	University of Illinois, Engineering Experiment Station Bulletin.
Ztschr. angew. Chem.	Zeitschrift für angewandte Chemie.
Ztschr. anorg. Chem.	Zeitschrift für anorganische Chemie.
Ztschr. Elektrochem.	Zeitschrift für Elektrochemie und angewandte physikalische Chemie.
Ztschr. ges. Kälte-Ind.	Zeitschrift für die gesamte Kälte-Industrie.
Ztschr. Metallkunde	Zeitschrift für Metallkunde.
Ztschr. physik. Chem.	Zeitschrift für physikalische Chemie.
Ztschr. wiss. Phot.	Zeitschrift für wissenschaftliche Photographie, Photophysik, und Photochemie.

BIBLIOGRAPHY[15]

1. AGLIARDI, N., AND SLODYK, T. (The Activated Adsorption of Sulfur Dioxide, Oxygen, and Mixtures of the Two on Vanadium Oxide.) Gazz. chim. ital., vol. 77, 1947, pp. 66-75; Chem. Abs., vol. 41, 1947, col. 7197.

2. APPLEBEY, M. P. The Recovery of Sulfur From Smelter Gases. Jour. Soc. Chem. Ind., vol. 56, 1937, pp. 139T-146T.

3. AYNSLEY, E. E., AND ROBINSON, P. L. The Kinetics of the Reaction Between Hydrogen and Sulfur. Part II. Jour. Chem. Soc., 1935, pp. 351-356.

4. BAERWALD, E., AND GOLDMANN, H. (Sulfur Trioxide From Sulfur Dioxide.) German Patent 537,763, Feb. 11, 1928.

5. BÄHR, H. (The Katasulf Process.) Glückauf, vol. 73, 1937, pp. 901-913.

6. BATTELLE MEMORIAL INSTITUTE. Economics of Fuel Gas From Coal. McGraw-Hill Book Co., Inc., New York, N. Y., 1950, 289 pp.

7. BAUKLOH, W., AND VALEA, I. (Effect of Sulfur Dioxide on Iron and Steel.) Korrosion u. Metallschutz, vol. 15, 1939, pp. 295-298.

8. BECKMAN, J. W. Method for Reducing Sulfur Compounds From Flue Gases. U. S. Patent 2,718,453, Sept. 20, 1955.

9. BERTHELOT, M. (Investigations on Electrolysis.) Compt. rend., vol. 93, 1881, pp. 757-762.

10. _____. (The Reactions Between Sulfur, Carbon, Their Oxides and Their Salts.) Compt. rend., vol. 96, 1883, pp. 298-304.

11. _____. (The Combustion of Hydrogen Mixed With an Oxygenated Gas.) Ann. chim. phys., vol. 14, (7), 1898, pp. 167-170; 289-293.

12. BILTZ, W., AND HÜLSMANN, O. (Low-Temperature Densities of Crystalline Nitric Acid, Sulfuric Acid, Phosphoric Acid, and Related Substances.) Ztschr. anorg. Chem., vol. 207, 1932, pp. 377-384.

13. BLEEKRODE, L. On the Experimental Determination of the Index of Refraction of Liquefied Gases. Proc. Roy. Soc. (London), vol. (A) 37, 1884, pp. 339-362.

14. BODENSTEIN, M., AND POHL, W. (Equilibrium Measurements on Contact Sulfuric Acid.) Ztschr. Elektrochem., vol. 11, 1905, pp. 373-384.

15. BODONI, D. (Recovery of Carbon Dioxide and Sulfur Dioxide From Combustion Gases.) Austrian Patent 174,896, May 11, 1953. Chem. Abs., vol. 47, 1953, col. 7780.

16. BOSWELL, M. C. Separating Sulfur Dioxide From Gaseous Mixtures. U. S. Patent 1,972,074, Sept. 4, 1934.

---

[15] Titles in parentheses are translations of the original title.

17. BOTTOMS, R. R. Organic Bases for Gas Purification. Ind. Eng. Chem., vol. 23, 1931, pp. 501-504.

18. BREWER, R. E., AND GHOSH, J. K. Desulfurization of Coal During Carbonization With Added Gases. Quantitative Determination of Sulfur Compounds. Ind. Eng. Chem., vol. 41, 1949, pp. 2044-2053.

19. BRINER, E., NICOLET, S., AND PAILLARD, H. (The Ozonization of Sulfurous Acid and Sulfur Dioxide. The Action of Ozone on the Participation of Oxygen in the Oxidation.) Helv. Chim. Acta, vol. 14, 1931, pp. 804-810.

20. BRINER, E., PAMM, G., AND PAILLARD, H. (The Velocity of Thermal Dissociation of the Sulfates of Calcium, Potassium and Sodium Alone or in the Presence of Added Materials; The Action Strongly Accelerated by Water Vapor.) Helv. Chim. Acta, vol. 32, 1949, pp. 635-646.

21. BRUNAUER, S. The Adsorption of Gases and Vapors. Vol. I, Princeton University Press, Princeton, N. J., 1943, 511 pp.

22. CARDOSO, E., AND FIORENTINO, U. (Experimental Researches on Some Thermal Properties of Gases. III. The Critical Constants and Vapor Pressures of Sulfur Dioxide.) Jour. chim. phys., vol. 23, 1926, pp. 841-847.

23. CARTER, B. M. Carbon Disulfide. U. S. Patent 2,141,740, Dec. 27, 1938.

24. CHAPMAN, W. R., AND RHYS JONES, D. C. The Removal of Sulfur From Coal. Jour. Inst. Fuel, vol. 28, 1955, pp. 102-108.

25. CHEMICAL ENGINEERING. Hi-Purity Liquid SO_2 From Roaster Gases. Vol. 60, No. 4, 1953, pp. 274-277.

26. CHEMICAL AND ENGINEERING NEWS. C and E N's Quarterly Report on Current Prices. Vol. 34, 1956, pp. 6387-6414.

27. _____. Coal Gets a Double Lift. Vol. 34, 1956, pp. 1318-1320.

28. CLARK, A. L., AND KATZ, L. Resonance Method of Measuring the Ratio of the Specific Heats of a Gas, Cp/Cv. III. Sulfur Dioxide and Nitrous Oxide. Canadian Jour. Res., vol. 19 (a), 1941, pp. 111-115. Recomputed by Woolley, H. W. Note on the Resonance Method of Measuring the Ratio of the Specific Heats of a Gas, Cp/Cv. Canadian Jour. Phys., vol. 31, 1953, pp. 604-612.

29. CLARK, L. M. The Effect of Gases on the Sintering of Lime. Rec. trav. Chim., vol. 68, 1949, pp. 969-982 (In English).

30. COEHN, A. (The Effect of Light on the Formation of Sulfuric Acid.) Ztschr. Elektrochem., vol. 13, 1907, pp. 545-548.

31. COEHN, A., AND BECKER, H. (Photochemistry of Sulfuric Acid.) Ztschr. physik. Chem., vol. 70, 1910, pp. 88-115. Also German Patent 217,722, July 9, 1907.

32. COPSON, R. L., AND PAYNE, J. W. Recovery of Sulfur Dioxide as Dilute Sulfuric Acid. Catalytic Oxidation in Water Solution. Ind. Eng. Chem., vol. 25, 1933, pp. 909-916.

33. COTTON, W. J. Nitrogen Oxide. U. S. Patent 2,485,476, Oct. 18, 1949.

34. CRABTREE, F., AND POWELL, A. R. Sulfur in Producer Gas. Bull. AIME, 1919, pp. 2687-2692.

35. CRAIG, D. N., AND VINAL, G. W. Solubility of Lead Sulfate in Solutions of Sulfuric Acid, Determined by Dithizone With a Photronic Cell. Nat. Bureau of Standards, Res. Jour., vol. 22, 1939, pp. 55-70.

36. CRAXFORD, S. R., POLL, A., AND WALKER, W. J. S. Recovery of Sulfur From Flue Gas by the Use of Ammonia. Jour. Inst. Fuel, vol. 25, 1952, pp. 13-14.

37. CRES, A. (Sulfur Trioxide.) French Patent 943,095, Feb. 25, 1949.

38. CRUSE, K. (EMF Measurements in Liquid Sulfur Dioxide.) Ztschr. Elektrochem., vol. 46, 1940, pp. 571-590.

39. DAVENPORT, S. J., AND MORGIS, G. G. Air Pollution - A Bibliography. Bureau of Mines Bull. 537, 1954, 448 pp.

40. DEAN, R. S., ST. CLAIR, H. W., AMBROSE, P. M., MARKS, G. W., AND WARTMAN, F. S. Fixation of Sulfur From Smelter Smoke. Bureau of Mines Rept. of Investigations 3339, 1937, 51 pp.

41. DESHMUKH, G. S., AND LAHIRY, B. Interaction of Sulfur Dioxide and Hydrogen Under Silent Electric Discharge. Jour. Indian Chem. Soc., vol. 26, 1949, pp. 257-261.

42. DICKINS, B. G. The Effect of Accommodation on Heat Conduction Through Gases. Proc. Roy. Soc. (London), vol. (A) 143, 1934, pp. 517-540.

43. DOUMANI, T. F., DEERY, R. F., AND BRADLEY, W. E. Recovery of Sulfur From Sulfur Dioxide in Waste Gases. Ind. Eng. Chem., vol. 36, 1944, pp. 329-332.

44. DOW, H. H., AND STROSACKER, C. J. Carbon Disulfide. U. S. Patent 1,350,858, Aug. 24, 1920.

45. DRUMILER, D. W., MOULTON, R. W., AND PUTNAM, G. L. Electrodeposition of Copper Powder From Acid Sulfate Baths. Ind. Eng. Chem., vol. 42, 1950, pp. 2099-2102.

46. DUECKER, W. W., AND EDDY, E. W. Sulfur. Min. Cong. Jour., vol. 42, 1956, pp. 65-67.

47. ECKMAN, J. R., AND ROSSINI, F. D. The Heat of Formation of Sulfur Dioxide. Nat. Bureau of Standards, Res. Jour., vol. 3, 1929, pp. 597-618.

48. ELBS, K. (Secondary Chemical Reactions in Electrolysis.) Ztschr. angew. Chem., vol. 16, 1903, pp. 290-292.

49. EVANS, W. H., AND WAGMAN, D. D. Thermodynamics of Some Simple Sulfur-Containing Molecules. Nat. Bureau of Standards, Res. Jour., vol. 49, 1952, pp. 141-148.

50. FAIRLIE, A. M. Sulfuric Acid Manufacture. Reinhold Publishing Corporation, New York, N. Y., 1936, 669 pp.

51. FEIGL, F. Spot Reaction Experiments. XI. Water as a Participant in Reactions of Sulfur Dioxide. Jour. Chem. Ed., vol. 22, 1945, pp. 558-560.

52. FETZER, W. R. The Electrolysis of Sodium Sulfide Solutions. Jour. Phys. Chem., vol. 32, 1928, pp. 1787-1807.

53. FICAI, C. (Adsorption of Sulfur Dioxide, Present in Small Percentages in Gaseous Mixtures, by Means of Colloidal Oxides and of Active Carbon.) Giorn. chim. ind. applicata, vol. 10, 1928, pp. 199-203; Chem. Abs., vol. 22, 1928, p. 3961.

54. FIELD, J. H., BRUNN, L. W., HAYNES, W. P., AND BENSON, H. E. Cost Estimates of Liquid Scrubbing Processes for Removal of Sulfur Dioxide From Flue Gases. Presented at Air Pollution Control Association Meeting, St. Louis, Missouri, June 3-6, 1957.

55. FISCHER, A., AND DELMARCEL, G. (The Electrolytic Oxidation of Sulfurous Acid in Aqueous Solution.) Bull. soc. chim. Belg., vol. 24, 1910, pp. 236-237.

56. FISKE, D. L. Thermal Properties of Sulfur Dioxide. Refrig. Eng., vol. 10, 1923, pp. 197-200, 204.

57. FLEMING, E. P., AND FITT, T. C. High-Purity Sulfur From Smelter Gases. Reduction With Natural Gas. Ind. Eng. Chem., vol. 42, 1950, pp. 2249-2253.

58. _____. Liquid Sulfur Dioxide From Waste Smelter Gases - Use of Dimethylaniline as Absorbent. Ind. Eng. Chem., vol. 42, 1950, pp. 2253-2258.

59. FOERSTER, F., AND FRIESSNER, A. (The Electrolysis of Aqueous Solutions With Platinized Anodes and the Electrolytic Formation of Dithionate.) Ber. deut. chem. Gesell., vol. 35, 1902, pp. 2515-2519.

60. FOERSTER, F., AND KUBEL, K. (Decomposition of Sulfites at High Heats.) Ztschr. anorg. Chem., vol. 139, 1924, pp. 261-292.

61. FOZ GAZULLA, O. R., AND SENENT PÉREZ, S. (Pressure Dependency of Thermal Conductivity and the Formation of Double Molecules of Sulfur Dioxide.) Ztschr. physik. Chem., vol. A-193, 1944, pp. 162-167.

62. FRANCIS, W., AND LEPPER, G. H. Recovery of Sulfur From Flue Gases. Engineering, vol. 172, 1951, pp. 36-37.

63. FRANCK, J., SPONER, H., AND TELLER, E. (Predissociation Spectra of Triatomic Molecules.) Ztschr. physik. Chem., vol. B-18, 1932, pp. 88-101.

64. FREI, E. (The Behavior of Manganese Salts at the Anode.) Dissertation, Giessen, 1901. Reported by Mellor, J. W. A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. XII, Longmans, Green and Company, London, 1932, 944 pp.

65. FREUNDLICH, H. Colloid and Capillary Chemistry. E. P. Dutton & Co., Inc., New York, N. Y., 1922, 883 pp.

66. FÜRSTENAU, R. (Specific Heat Ratios of Gases and Their Temperature Dependency.) Ann. Physik, vol. 27, 1908, pp. 735-772.

67. FURUFUJI, I. (Treatment of Sulfur Dioxide in Flue Gas.) Japanese Patent 174,880, June 6, 1948; Chem. Abs., vol. 43, 1949, col. 7201.

68. GAMSON, B. W., AND ELKINS, R. H. Sulfur From Hydrogen Sulfide. Chem. Eng. Progress, vol. 49, 1953, pp. 203-215.

69. GENEREAUX, R. P. Viscosity Data in Graphical Form. Ind. Eng. Chem., vol. 22, 1930, pp. 1382-1385.

70. GIAUQUE, W. F., AND STEPHENSON, C. C. Sulfur Dioxide. The Heat Capacity of Solid and Liquid. Vapor Pressure. Heat of Vaporization. The Entropy Values From Thermal and Molecular Data. Jour. Am. Chem. Soc., vol. 60, 1938, pp. 1389-1394.

71. GLADSTONE, J. H., AND TRIBE, A. The Chemistry of the Planté and Faure Accumulators. I. Local Action. Nature, vol. 25, 1882, pp. 221-223.

72. _____. The Chemistry of the Planté and Faure Accumulators. II. The Charging of the Cell. Nature, vol. 25, 1882, pp. 461-463.

73. _____. The Chemistry of the Planté and Faure Accumulators. III. The Discharge of the Cell. Nature, vol. 26, 1882, pp. 251-252.

74. _____. The Chemistry of the Planté and Faure Accumulators. IV. The Function of Sulfate of Lead, Nature, vol. 26, 1882, pp. 602-603.

75. _____. The Chemistry of the Planté and Faure Accumulators. Nature, vol. 27, 1883, pp. 583-584.

76. GLASSTONE, S. An Introduction to Electrochemistry. D. Van Nostrand Co., Inc., New York, N. Y., 1942, 557 pp.

77. GLASSTONE, S., AND HICKLING, A. Studies in Electrolytic Oxidation. I. The Electrolytic Oxidation of Sodium Thiosulfate at a Platinum Anode. Jour. Chem. Soc., 1932, pp. 2345-2356.

78. _____. Studies in Electrolytic Oxidation. II. Further Experiments on the Electrolytic Oxidation of Sodium Thiosulfate. Jour. Chem. Soc., 1932, pp. 2800-2807.

79. _____. Studies in Electrolytic Oxidation. III. The Formation of Dithionate by the Electrolytic Oxidation of Potassium Sulfite. Jour. Chem. Soc., 1933, pp. 829-836.

80. _____. Electrolytic Oxidation and Reduction. D. Van Nostrand Co., Inc., New York, N. Y., 1936, 420 pp.

81. _____. The Hydrogen Peroxide Theory of Electrolytic Oxidation. Chem. Rev., vol. 25, 1939, pp. 407-441.

82. GLOCKLER, G., AND LIND, S. C. The Electrochemistry of Gases and Other Dielectrics. J. Wiley & Sons, Inc., New York, N. Y., 1939, 469 pp.

83. GMELINS HANDBOOK OF INORGANIC CHEMISTRY. (System 9, Sulfur, A-2. Occurrence - Technology of Sulfur and Its Compounds - Colloidal Sulfur - Physiological Damage.) 1953, Verlag Chemie, G.m.b.H., Weinheim, Germany, 510 pp.

84. _____. (System 9, Sulfur, B-1 - Hydrides and Oxides of Sulfur.) 1953, Verlag Chemie, G.m.b.H., Weinheim, Germany, 372 pp.

85. GORDON, A. R. The Free Energy of Sulfur Dioxide. Jour. Chem. Phys., vol. 3, 1935, pp. 336-337.

86. GRAFF, R. A. Sulfur From Petroleum Gases. Oil Gas Jour., vol. (42) 47, 1949, pp. 99-104.

87. GREENBURG, L., AND JACOBS, M. B. Sulfur Dioxide in New York City Atmosphere. Ind. Eng. Chem., vol. 48, 1956, pp. 1517-1521.

88. GRIFFITH, R. H., AND HILL, S. G. The Hydrogenation of Simple Sulfur Compounds. Part I. Nickel Subsulfide as a Catalyst. Jour. Chem. Soc., 1938, pp. 717-720.

89. GRODZOVSKIĬ, M. K. (Mechanism of the Catalytic Oxidation of Sulfur Dioxide in a Solution of Manganese Salts. II. Action of Ozone on Solutions of Manganous Salts.) Jour. Phys. Chem. [U.S.S.R.], vol. 6, 1935, pp. 496-510; Chem. Abs., vol. 30, 1936, col. 2091.

90. GRÜNERT, E. (Desulfurization of Coal.) Jour. prakt. Chem., vol. 122, 1929, pp. 1-120.

91. HAMMICK, D. L. The Action of Sulfur Dioxide on Metal Oxides. Jour. Chem. Soc., vol. 111, 1917, pp. 379-389.

92. HATFIELD, W. H. Heat-Resisting Steels. Jour. Iron and Steel Inst., vol. 115, 1927, pp. 483-508.

93. HEDVALL, J. A. (The Action of Gases That are Inactive in the Ordinary Sense on the Chemical Activity of Solid Materials.) Iva, No. 1, 1942, pp. 3-19; Chem. Abs., vol. 37, 1943, col. 4949.

94. HEWSON, G. W., PEARCE, S. L., POLLITT, A., AND REES, R. L. The Application to the Battersea Power Station of Researches Into the Elimination of Noxious Constituents From Flue Gases, and the Treatment of Resulting Effluents. Jour. Soc. Chem. Ind. (Proc.), vol. 15, 1933, pp. 67-99.

95. HEYN, E., AND BAUER, O. (Copper and Sulfur.) Metallurgie, vol. 3, 1906, pp. 73-86.

96. HILL, R. A. The Photochemical Decomposition of Gaseous Sulfur Dioxide. Trans. Faraday Soc., vol. 20, 1924, pp. 107-112.

97. HIXSON, A. W., AND MILLER, R. Recovery of Acidic Gases. U. S. Patent 2,449,537, Sept. 21, 1948.

98. HOFMAN, H. O., AND WANJUKOW, W. The Decomposition of Metallic Sulfates at Elevated Temperatures in a Current of Dry Air. Trans. AIME, vol. 43, 1913, pp. 523-577.

99. HUFF, W. J., AND LOGAN, L. The Purification of Commercial Gases at Elevated Temperatures. Am. Gas Assoc., Proc., vol. 18, 1936, pp. 724-756.

100. HUXLEY, H., AND LOWERY, H. The Refraction and Dispersion of Sulfuretted Hydrogen, Sulfur Dioxide, and Carbon Oxysulfide. Proc. Roy. Soc. (London), vol. A-182, 1943, pp. 207-216.

101. INTERNATIONAL CRITICAL TABLES. Numerical Data, Physics, Chemistry and Technology. Vol. III, McGraw-Hill Book Company, Inc., New York, N. Y., 1928, 444 pp.

102. JACKSON, A., AND SOLBETT, J. M. Sulfuric Acid Plant: Tail Gas Treatment. Chem. and Ind., 1955, pp. 1304-1311.

103. JELLINEK, K. (The Electrolytic Preparation of Hyposulfite From Bisulfite Solution.) Ztschr. Elektrochem., vol. 17, 1911, pp. 245-261.

104. JOHNSTONE, H. F. Metallic Ions as Catalysts For the Removal of Sulfur Dioxide From Boiler Furnace Gases. Ind. Eng. Chem., vol. 23, 1931, pp. 559-561.

105. _____. Progress in the Removal of Sulfur Compounds From Waste Gases. Combustion, vol. 5, No. 2, 1933, pp. 19-30.

106. _____. Recovery of Sulfur Dioxide From Dilute Gases. Pulp & Paper Mag. Canada, vol. 53, Mar. 1952, pp. 105-112.

107. JOHNSTONE, H. F., READ, H. J., AND BLANKMEYER, H. C. Recovery of Sulfur Dioxide From Waste Gases. Equilibrium Vapor Pressures Over Sulfite-Bisulfite Solutions. Ind. Eng. Chem., vol. 30, 1938, pp. 101-109.

108. JOHNSTONE, H. F., AND SINGH, A. D. The Recovery of Sulfur Dioxide From Dilute Waste Gases by Chemical Regeneration of the Absorbent. Univ. Illinois, Eng. Exper. Stat. Bull., 324, 1940, 137 pp.

109. JONES, J. H., KING, J. G., AND SINNATT, F. S. The Reactivity of Coke. 3. The Influence of Iron Compounds. Technical Paper 25. Great Britain Fuel Research Board, Technical Papers 21-28, 1929-30.

110. JOSHI, S. S., AND SHARMA, K. K. (The Decomposition of Sulfur Dioxide by an Electric Discharge.) Jour. chim. phys., vol. 31, 1934, pp. 511-516; Chem. Abs., vol. 29, 1935, col. 1721.

111. KANE, L. J., AND SINGH, A. D. Fluidized Devolatilization of Coal for Power Plant Practice. Trans. ASME, vol. 70, 1948, pp. 957-964.

112. KARDOS, A. (Thermal Conductivities of Various Liquids.) Ztschr. ges. Kälte-Ind., vol. 41, 1934, pp. 1-6, 29-35.

113. KASTENS, M. L., AND HUTCHINSON, J. C. Contact Sulfuric Acid From Sulfur. Ind. Eng. Chem., vol. 40, 1948, pp. 1340-1349.

114. KATZ, M., AND COLE, R. J. Recovery of Sulfur Compounds From Atmospheric Contaminants. Ind. Eng. Chem., vol. 42, 1950, pp. 2258-2269.

115. KELLEY, K. K. Contributions To The Data On Theoretical Metallurgy. VII. The Thermodynamic Properties of Sulfur and Its Inorganic Compounds. Bureau of Mines Bull. 406, 1937, 154 pp.

116. KEPPELER, G. (Studies on the Iron Oxide Contact Process.) Ztschr. angew. Chem., vol. 21, 1908, pp. 577-589.

117. KING, R. A. Economic Utilization of Sulfur Dioxide From Metallurgical Gases. Ind. Eng. Chem., vol. 42, 1950, pp. 2241-2248.

118. KLEMENC, A. (Urea Formation in the System CO_2-NH_3 and COS-NH_3.) Ztschr. anorg. Chem., vol. 191, 1930, pp. 246-282.

119. KNIETSCH, R. (Sulfuric Acid and Its Production by the Contact Process.) Ber. deut. chem. Gesell., vol. 34, 1901, pp. 4069-4115.

120. KORNFELD, G. The Primary Process of Photodissociation in Sulfur Trioxide. Trans. Faraday Soc., vol. 33, 1937, pp. 614-617.

121. KORNFELD, G., AND McCAIG, M. The Photochemical Decomposition of Sulfur Dioxide. Trans. Faraday Soc., vol. 30, 1934, pp. 991-994.

122. KORNFELD, G., AND WEEGMANN, E. (The Oxidation of Sulfur Dioxide in Ultraviolet Light.) Ztschr. Elektrochem., vol. 36, 1930, pp. 789-794.

123. KOSTER, W. R. Inorganic Chemicals. Chem. Eng. News, vol. 34, 1956, pp. 5669-5677.

124. KUDRA, O. K., AND IVANOV, K. N. Oxidation Processes at the Cathode. Jour. Phys. Chem., vol. 40, 1936, pp. 769-777.

125. LANGE, A. (On Some Properties of Liquid Sulfur Dioxide.) Ztschr. angew. Chem., vol. 12, 1899, pp. 275-277, 300-305.

126. LANGMUIR, I. The Constitution and Fundamental Properties of Solids and Liquids. Jour. Am. Chem. Soc., vol. 38, 1916, pp. 2221-2295.

127. LATIMER, W. M., AND HILDEBRAND, J. H. Reference Book of Inorganic Chemistry. The Macmillan Company, New York, N. Y., 1951, 625 pp.

128. LEDUC, A. (Coefficients of Expansion of Gases. Applications. Internal Pressure and Internal Work. The Experiments of Kelvin and Joule. Perfect State of True Gases.) Ann. phys., vol. (9) 5, 1916, pp. 180-217.

129. LEE, J. A. Sulfur From Arkansas Sour Gas. Chem. Met. Eng., vol. 49, No. 6, 1942, pp. 80-82.

130. LEPSOE, R. Chemistry of Sulfur Dioxide Reduction - Thermodynamics. Ind. Eng. Chem., vol. 30, 1938, pp. 92-100.

131. _____. Chemistry of Sulfur Dioxide Reduction. Kinetics. Ind. Eng. Chem., vol. 32, 1940, pp. 910-918.

132. LOSANITSCH, S. M. (Electrosyntheses.) Ber. deut. chem. Gesell., vol. 40, 1907, pp. 4656-4666.

133. LOWENSTEIN-LOM, W. G. Removal of Sulfur Oxides From Flue Gases and Their Conversion to Ammonium Sulfate. British Patent 708,095, Apr. 28, 1954.

134. LOWRY, H. H. (editor). Chemistry of Coal Utilization. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1945, 920 pp.

135. MAGILL, P. L., HOLDEN, F. R., AND ACKLEY, C. (editors). Air Pollution Handbook. McGraw-Hill Book Company, Inc., New York, N. Y., 1956.

136. MAHANT, S. D. The Oxidation of Sulfur Dioxide in the Electrodeless Discharge. Jour. Indian Chem. Soc., vol. 9, 1932, pp. 417-422.

137. MALLETTE, F. S. (editor). Problems and Control of Air Pollution. Reinhold Publishing Corporation, New York, N. Y., 1955, 280 pp.

138. MANTELL, C. L. Adsorption. McGraw-Hill Book Company, New York, N. Y., 1945, 386 pp.

139. _____. Industrial Electrochemistry. McGraw-Hill Book Company, New York, N. Y., 1950, 781 pp.

140. MANUFACTURING CHEMISTS' ASSOCIATION, INC. Air Pollution Abatement Manual, Washington, D. C., 1952.

141. MARCHAL, G. (Thermal Decomposition of Sulfates.) Jour. chim. phys., vol. 22, 1925, pp. 559-582.

142. MARINO, L. (The Existence of a New Type of Dioxide.) Gazz. chim. ital., vol. 38:1, 1908, pp. 249-279.

143. McCABE, L. C. (chairman). Air Pollution, Proceedings of the United States Technical Conference on Air Pollution. McGraw-Hill Book Company, Inc., New York, N. Y., 1952, 847 pp.

144. McELROY, K. P. Carbon Disulfide. U. S. Patent 1,369,825, Mar. 1, 1921.

145. McGAVACK, J., AND PATRICK, W. A. The Adsorption of Sulfur Dioxide by the Gel of Silicic Acid. Jour. Am. Chem. Soc., vol. 42, 1920, pp. 946-978.

146. MEETHAM, A. R. Atmospheric Pollution. Its Origins and Prevention. Pergamon Press, Inc., New York, N. Y., 1956, 302 pp.

147. MEYER, R. J., AND RÖTGERS, K. (The Dissociation Temperatures of MnO_2 and Mn_2O_3 in Air and Oxygen.) Ztschr. anorg. Chem., vol. 57, 1908, pp. 104-112.

148. MILES, F. D. The Manufacture of Sulfuric Acid. (Contact Process.) D. Van Nostrand Company, Inc., New York, N. Y., 1925.

149. MILLAR, R. W. The Specific Heats at Low Temperatures of Manganous Oxide, Manganous-Manganic Oxide and Manganese Dioxide. Jour. Am. Chem. Soc., vol. 50, 1928, pp. 1875-1883.

150. MILLER, E. B. Adsorption by Silica Gel. Chem. Met. Eng., vol. 23, 1920, pp. 1155-1160, 1219-1222, 1251-1254.

151. MILLS, T., AND EVANS, U. R. The Effect of Sulfur Dioxide on the Oxidation of Copper. Jour. Chem. Soc., 1956, pp. 2182-2196.

152. MITCHELL, D. R. (editor). Coal Preparation. The American Institute of Mining and Metallurgical Engineers, New York, N. Y., 1950, 830 pp.

153. MOLES, E., TORAL, T., AND ESCRIBANO, A. Limiting Densities and Molecular Weights of Oxygen, Carbon Dioxide, Sulfur Dioxide and Hydrogen Sulfide. Atomic Weights for Carbon and Sulfur. Trans. Faraday Soc., vol. 35, 1939, pp. 1439-1452.

154. MOND, L., RAMSAY, W., AND SHIELDS, J. On the Occlusion of Oxygen and Hydrogen by Platinum Black. Trans. Roy. Soc. (London), vol. A190, 1897, pp. 129-153.

155. MONKHOUSE, A. C., AND NEWALL, H. E. Industrial Gases - Recovery of Sulfur Dioxide. Delivered at the Society of Chemical Industries Conference at Sheffield, 1956.

156. MOORE, T. E., ELLIS, M., AND SELWOOD, P. W. Solid Oxides and Hydroxides of Manganese. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 856-866.

157. NEUMANN, B. (The Reaction Mechanism in the Contact Sulfuric Acid Process and the Method of Action of Activators.) Ztschr. Elektrochem., vol. 35, 1929, pp. 42-51.

158. _____. (Sulfuric Acid Catalysis.) Ztschr. Elektrochem., vol. 38, 1932, pp. 304-311.

159. NEUMANN, B., AND GOEBEL, E. (The Adsorption of Sulfur Dioxide on Platinum, Iron Oxide, and Chromium Oxide.) Ztschr. Elektrochem., vol. 39, 1933, pp. 352-362, 672-682.

160. _____. (The Adsorption of Sulfur Dioxide on Vanadium Pentoxide.) Ztschr. Elektrochem., vol. 40, 1934, pp. 764-765.

161. NEUMANN, B., AND KUNZ, H. (The Reaction in the Hargreaves Process.) Ztschr. angew. Chem., vol. 42, 1929, pp. 1085-1087.

162. NEWALL, H. E. The Ammonia Process for the Removal of Sulfur Dioxide From Flue Gas. Pres. 1st Internat. Cong. on Air Pollution, ASME, New York, N. Y., Mar. 1-2, 1955, Paper 55-APC-3.

163. NONHEBEL, G. A Commercial Plant for the Removal of Smoke and Oxides of Sulfur From Flue Gases. Trans. Faraday Soc., vol. 32, 1936, pp. 1291-1296.

164. NYROP, J. E. (Gaseous Reactions.) Danish Patent 54,170, Jan. 17, 1938, Chem. Abs., vol. 32, 1938, col. 2852.

165. OLIVE, T. R. Modern Chemical Engineering Revamps Conventional Contact Process. Chem. Eng., vol. 57, 1950, pp. 103-107.

166. ONTARIO RESEARCH FOUNDATION. The Removal of Sulfur Gases From Smelter Fumes. Baptist Johnson, Publisher, Toronto, Canada, 1949, 149 pp.

167. OWEN, A. J., SYKES, K. W., AND THOMAS, D. J. D. Thermodynamics of Carbon Disulfide Synthesis. Equilibrium in Some Reactions Involving Hydrogen Sulfide, Sulfur Dioxide, Carbon Dioxide and Carbon. Trans. Faraday Soc., vol. 47, 1951, pp. 419-428.

168. PARRY, V. F., LANDERS, W. S., AND WAGNER, E. O. Low-Temperature Carbonization of Lignite and Noncoking Coals in the Entrained State. Min. Eng., vol. 8, 1956, pp. 54-64.

169. PASCAL, P. (Magnetic Properties of Some Easily Liquefiable Gases.) Compt. rend., vol. 148, 1909, pp. 413-415.

170. PEARSON, J. L., NONHEBEL, G., AND ULANDER, P. H. N. The Removal of Smoke and Acid Constituents From Flue Gases by a Non-Effluent Water Process. Jour. Inst. Fuel, vol. 8, 1935, pp. 119-156.

171. PERLICK, A. (Calorimetric Measurements of Sulfur Dioxide, Methylene Chloride, Difluormonochlorethane and Tetrafluordichlorethane.) Ztschr. ges. Kälte-Ind., vol. 44, 1937, pp. 201-206.

172. PERRY, J. H. Adsorption of Vapors by Ferric Hydroxide Gel. Ind. Eng. Chem., vol. 19, 1927, pp. 746-748.

173. _____. (editor). Chemical Engineers' Handbook. McGraw-Hill Book Company, New York, N. Y., 1950, 1942 pp.

174. PICKERING, S. F. A Review of the Literature Relating to the Critical Constants of Various Gases. Nat. Bureau of Standards, Sci. Papers 541, vol. 21, 1926, pp. 597-629.

175. PLUMMER, A. W. Thermodynamic Data for System SO_2-H_2O, Bibliography and Critical Analysis. Chem. Eng. Progress, vol. 46, 1950, pp. 369-374.

176. P'YANKOV, V. A. (Absorption of Hydrogen Sulfide and Sulfur Dioxide From an Air Current.) Jour. Gen. Chem. (U.S.S.R.), vol. 5, 1935, pp. 1112-1118; Chem. Abs., vol. 30, 1936, col. 927.

177. RANDALL, M., NIELSEN, R. F., AND WEST, G. H. Free Energy of Some Copper Compounds. Ind. Eng. Chem., vol. 23, 1931, pp. 388-400.

178. RASSOW, B., AND HOFFMANN, K. (The Formation of Carbon Disulfide by the Interaction of Sulfur Dioxide and Charcoal.) Jour. prakt. Chem., vol. 104, 1922, pp. 207-240.

179. RAVITZ, S. F., WYMAN, W. F., BACK, A. E., AND TAME, K. E. The Dithionate Process for Recovery of Manganese From Low-Grade Ores. AIME, Tech. Pub. 2064. Metals Technol., Sept. 1946, 10 pp.

180. REES, R. L. The Removal of Sulfur Dioxide From Power-Plant Stack Gases. Pres. before 1st Internat. Cong. on Air Pollution, ASME, New York, N. Y., Mar. 1-2, 1955, Paper 55-APC-2.

181. REINDERS, W., AND GOUDRIAAN, F. (The Roasting of Copper; Equilibrium in the System Cu-S-O.) Ztschr. anorg. Chem., vol. 126, 1923, pp. 85-103.

182. REMY, H., AND HENE, W. (The Adsorption of Gases by Active Charcoal.) Kolloid-Ztschr., vol. 61, 1932, pp. 313-322.

183. REPORT OF THE FUEL RESEARCH BOARD, 1946 TO 1949. Department of Scientific and Industrial Research, London. Her Majesty's Stationery Office, 1951.

184. REPORT OF THE FUEL RESEARCH BOARD, 1951. Department of Scientific and Industrial Research, London. Her Majesty's Stationery Office, 1952.

185. REYERSON, L. H., AND SWEARINGEN, L. E. The Adsorption of Gases by Metallized Silica Gels. Jour. Phys. Chem., vol. 31, 1927, pp. 88-101.

186. RIESENFELD, E. H. (Sulfuric Anhydride.) German Patent 229,274, May 13, 1909.

187. RIESENFELD, E. H., AND HESSE, M. (Preparation of Sulfur and Sulfuric Acid From Sulfates of the Alkaline Earths. 5. The Decomposition of Calcium Sulfide by Steam and the Direct Conversion of Gypsum and Anhydrite into Oxide.) Jour. prakt. Chem., vol. 100, 1920, pp. 154-158.

188. ROBERSON, A. H., AND MARKS, G. W. Fixation of Sulfur From Smelter Smoke. Partial Pressures of Sulfur Dioxide Over Solutions of Sulfur Dioxide in Mixtures of Water and Various Aliphatic Amines. Bureau of Mines Rept. of Investigations 3415, 1938, 45 pp.

189. ROBINSON, C. S. The Recovery of Vapors. Reinhold Publishing Corporation, New York, N. Y., 1942, 273 pp.

190. ROSE, H. (The Dispersion and Rotatory Dispersion of Optically Active Crystals.) Neues Jahrb. Min. Geol., (Beil. Bd.), vol. 29, 1910, pp. 53-105.

191. ROSSINI, F. D., WAGMAN, D. D., EVANS, W. H., LEVINE, S., AND JAFFE, I. Selected Values of Chemical Thermodynamic Properties. Nat. Bureau of Standards, Circ., 500, 1952, 1268 pp.

192. RUSSELL, E. J., AND SMITH, N. The Combination of Sulfur Dioxide and Oxygen. Jour. Chem. Soc., vol. 77, 1900, pp. 340-352.

193. RYNNING, D. F., AND HURD, C. O. Thermodynamic Properties of Sulfur Dioxide. Trans. AICE, vol. 41, 1945, pp. 265-281.

194. SANDS, A. E., WAINWRIGHT, H. W., AND EGLESON, G. C. Organic Sulfur in Synthesis Gas: Occurrence, Determination, and Removal. Bureau of Mines Rept. of Investigations 4699, 1950, 51 pp.

195. SCHAUFELBERGER, F. A. Precipitation of Metal From Salt Solution by Reduction With Hydrogen. Jour. Metals, vol. 8, 1956, pp. 695-704.

196. SCHENCK, R., AND KEUTH, H. (The Displacement of Chemical Equilibrium States as Research Aid; Illustrated in the Copper-Roasting Reaction.) Ztschr. Elektrochem., vol. 46, 1940, pp. 298-308.

197. SCHENCK, R., AND RAUB, E. (Equilibrium Studies in the Systems Co-S-O and Ni-S-O.) Ztschr. anorg. Chem., vol. 178, 1929, pp. 225-251.

198. SCHENK, P. W. (The Chemistry of the Lower Oxides of Sulfur.) Chem-Ztg., vol. 67, 1943, pp. 251-253, 273-276.

199. SCHNEIDER, A., AND ESCH, U. (The Reactions Between Magnesium and Sulfur Dioxide.) Ztschr. Metallkunde, vol. 32, 1940, pp. 173-177.

200. _____. (The Solubility of Sulfur Dioxide in Liquid Magnesium.) Ztschr. Metallkunde, vol. 32, 1940, pp. 177-184.

201. SCHOENFELD, F. (Absorption Coefficients of Sulfur Dioxide, Chlorine, and Hydrogen Sulfide.) Ann. Chem., Justus Liebigs, vol. 95, 1855, pp. 1-23.

202. SEIL, G. E. Gas Chemists' Manual of Dry Box Purification of Gas With an Annotated Bibliography. Am. Gas Assoc., Inc., New York, N. Y., 1943, 284 pp.

203. SEYER, W. F., ASSALY, T. C., AND LEITH, J. A. The Reaction of Sulfur Dioxide, Water, and Oxygen in an Electrolytic Cell. Trans. Electrochem. Soc., vol. 91, 1947, pp. 133-146.

204. SEYER, W. F., AND PECK, W. S. The Effect of Temperature On The Molecular Surface Energy of Binary Mixtures. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 14-23.

205. SHERWOOD, T. K., AND PIGFORD, R. L. Absorption and Extraction. 2d ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1952, 478 pp.

206. SHIELS, D. O. The Adsorption of Sulfur Dioxide by Platinized Asbestos. Jour. Phys. Chem., vol. 33, 1929, pp. 1167-1174.

207. _____. The Adsorption of Sulfur Dioxide by Platinum Black. Jour. Phys. Chem., vol. 33, 1929, pp. 1175-1183.

208. SILLER, C. W. Carbon Disulfide From Sulfur Dioxide and Anthracite. Ind. Eng. Chem., vol. 40, 1948, pp. 1227-1233.

209. SIMON, A., AND FEHÉR, F. (Oxides of Manganese.) Ztschr. Elektrochem., vol. 38, 1932, pp. 137-148.

210. SIMON-CARVES, LTD. Removal of Sulfur Compounds From Boiler Flue Gases. British Patent 525,883, Sept. 6, 1940.

211. SMALLEY, G. E., and Klohr, J. W. Refinery Sulfur Recovery Aids Air Pollution Control. Pres. 1st Internat. Cong. on Air Pollution, Mar. 1-2, New York, N. Y., 1955, Paper 55-APC-12.

212. SNOW, R. D. Conversion of Coal Sulfur to Volatile Sulfur Compounds During Carbonization in Streams of Gases. Ind. Eng. Chem., vol. 24, 1932, pp. 903-909.

213. SNOWBALL, A. F. A Cyclic Process of Sulfuric Acid Manufacture at Trail, B. C. Canadian Chem. Process Ind., vol. 31, 1947, pp. 1110-1114.

214. STAKELBECK, H. (The Viscosities of Various Refrigerants in the Liquid and Vapor States and Their Dependence on Pressure and Temperature.) Ztschr. ges. Kälte-Ind., vol. 40, 1933, pp. 33-40.

215. STOUGHTON, B., AND BUTTS, A. Engineering Metallurgy. McGraw-Hill Book Co., Inc., New York, N. Y., 1938, 525 pp.

216. STOURDZÉ VISCONTI, Y. (Obtaining Elementary Sulfur. The Catalytic Property of Vanadium Oxide in the Reduction of Sulfurous Gas by Carbon Monoxide.) Rev. quím. ind., vol. 14, No. 163, 1945, pp. 22-26; Chem. Abs., vol. 40, 1946, col. 5212.

217. STUBBS, C. M. The Action of Sulfur Dioxide on Copper at High Temperatures. Jour. Chem. Soc., vol. 103, 1913, pp. 1445-1461.

218. TAINTON, U. C., AND BOSQUI, D. The Electrolytic Zinc Plant of the Evans-Wallower Zinc Company at East St. Louis, Ill. Trans. Electrochem. Soc., vol. 57, 1930, pp. 241-253.

219. TARBUTTON, G., DRISKELL, J. C., JONES, T. M., GRAY, F. J., AND SMITH, C. M. Recovery of Sulfur Dioxide From Flue Gases. Ind. Eng. Chem., vol. 49, 1957, pp. 392-395.

220. TERN, R. (Sulfur Trioxide.) French Patent 650,684, Mar. 9, 1928.

221. THOMPSON, M. de K., AND THOMPSON, N. J. The Electrolytic Oxidation of Sulfurous Acid. Met. Chem. Eng., vol. 15, 1916, pp. 677-679.

222. TILDEN, W. A. The Specific Heats of Metals, and the Relation of Specific Heat to Atomic Weight. Trans. Roy. Soc. (London), vol. (A) 194, 1900, pp. 233-255.

223. TOCCO, L. Promoting Chemical Reactions by Electric Fields. British Patent 330,226, Nov. 7, 1928.

224. TOMKINSON, M. G. (Catalytic Hydrogenation of Sulfur Dioxide.) Compt. rend., vol. 176, 1923, pp. 35-36.

225. TRAENCKNER, K. Pulverized-Coal Gasification Ruhrgas Processes, Trans. ASME, vol. 75, 1953, pp. 1095-1101.

226. TRAUTZ, M., AND HELFRICH, F. (Influence of Impurities and Applicability of the Mass-Action Law in the Light Reaction $2SO_2 + O_2 = 2SO_3$.) Ztschr. wiss. Phot., vol. 33, 1934, pp. 111-122.

227. TRAUTZ, M., AND PAKSCHWER, S. (The Sulfide-Sulfate Reaction.) Jour. prakt. Chem., vol. 122, 1929, pp. 147-181.

228. VEDENSKY, D. N. How the SO_2 Process Worked on Three Kids Manganese Ore. Eng. Min. Jour., vol. 147, July 1946, pp. 58-64.

229. VELEY, V. H. The Inertness of Quicklime. Jour. Chem. Soc., vol. 63, 1893, pp. 821-833.

230. VERNON, W. H. J. A Laboratory Study of the Atmospheric Corrosion of Metals. Part I. The Corrosion of Copper in Certain Synthetic Atmospheres, With Particular Reference to the Influence of Sulfur Dioxide in Air of Various Relative Humidities. Trans. Faraday Soc., vol. 27, 1931, pp. 255-277.

231. VIERK, A. L. (The Measurement of the Dielectric Constants of Liquid SO_2 at Normal Pressure From -16.5° to -68.8° C.) Ztschr. anorg. Chem., vol. 261, 1950, pp. 279-282.

232. VINAL, G. W. Storage Batteries. John Wiley & Sons, Inc., New York, N. Y., 1955, 446 pp.

233. WALKER, S. W. Hydrogen Sulfide From Sulfur Dioxide and Methane. Ind. Eng. Chem., vol. 38, 1946, pp. 906-912.

234. WALLIS, E. Atmospheric Pollution and the Zinc Industry. Chem. & Ind., 1955, pp. 1271-1273.

235. WASILEWSKI, L., AND KOBYLCZYK, A. (Production of Ammonium Persulfate.) Przemysl Chem., vol. 11 (34), No. 5, 1955, p. 241; abs. in Ind. Chemist, vol. 31, 1955, pp. 575-576.

236. WEIDMANN, H., AND ROESNER, G. (Process for the Manufacture of Pure Sulfur Dioxide.) Metallges., Periodic Rev., vol. 11, 1936, pp. 7-13; see also Ind. Eng. Chem., news ed., vol. 14, 1936, p. 105.

237. WHITNEY, R. P., HAN, S. T., AND DAVIS, J. L. The Mechanism of Sulfur Dioxide Absorption in Aqueous Media. TAPPI, vol. 36, 1953, pp. 172-175.

238. WICHERS, E. Report on Atomic Weights for 1954-55. Jour. Am. Chem. Soc., vol. 78, 1956, pp. 3235-3240.

239. WIELAND, K. Thermo-Optical Dissociation of Sulfur Dioxide. Trans. Faraday Soc., vol. 30, 1934, pp. 260-265.

240. WILSDON, B. H., AND McCONNELL, F. J. The Measurement of Atmospheric Sulfur Pollution by Means of Lead Peroxide. Jour. Soc. Chem. Ind., vol. 53, 1934, pp. 385T-388T.

241. WILSON, R. E. Note on the Adsorption of Nitrogen and Oxygen by Charcoal. Phys. Rev., vol. 16, 1920, pp. 8-16.

242. WÖHLER, F., AND MAHLA, F. (Observations on the Formation of Sulfuric Acid From Sulfurous Acid and Oxygen.) Ann. Chem., Justus Liebigs, vol. 81, 1852, pp. 255-256.

243. WOOLLAM, J. P. V., AND JACKSON, A. The Removal of Oxides of Sulfur From Exit Gases. Soc. Chem. Ind. (London), Chem. Eng. Group Proc., vol. 27, 1945, pp. 43-51.

244. YANCEY, H. F., AND PARR, S. W. Sulfur Forms in Coal - Distribution and Control. Ind. Eng. Chem., vol. 16, 1924, pp. 501-508.

245. YOUNG, S. W. The Thiogen Process for Removing Sulfur Fumes. Trans. AICE, vol. 8, 1915, pp. 81-89.

246. YUSHKEVICH, N. F., AND KARZHAVIN, V. A. (Manufacture of Sulfur From Sulfurous Gas Obtained as a Byproduct in Refining Metals.) Jour. Chem. Ind., (U.S.S.R.) vol. 2, 1926, pp. 474-478, 559-563, 719-726; Chem. Abs., vol. 20, 1926, pp. 3335, 3782.

247. **YUSHKEVICH, N. F., KARZHAVIN, V. A., AND AVDEEVA, A. V.** (The Preparation of Sulfur From Sulfur Dioxide.) Jour. Chem. Ind. (U.S.S.R.) No. 3, 1932, pp. 17-26; Chem. Abs., vol. 26, 1932, p. 4685.

248. **YUSHKEVICH, N. F., KARZHAVIN, V. A., AVDEEVA, A. V., AND KRECHEMOV, T. T.** (The Preparation of Sulfur From Sulfur Dioxide. VII. The Reaction Between Sulfur Dioxide and Hydrogen.) Jour. Chem. Ind. (U.S.S.R.), No. 8, 1933, pp. 50-58; Chem. Abs., vol. 28, 1934, col. 1474.

249. **YUSHKEVICH, N. F., KARZHAVIN, V. A., AVDEEVA, A. V., AND NICOL'SKAYA, Y. P.** (Preparation of Sulfur From Sulfur Dioxide. VIII. The Reaction of Sulfur Dioxide With Hydrocarbons.) Jour. Chem. Ind. (U.S.S.R.), No. 2, 1934, pp. 33-37; Chem. Abs., vol. 28, 1934, col. 3845.

250. **ZAHN, C. T.** The Electric Moment of CO_2, NH_3, and SO_2. Phys. Rev., vol. 27 (2), 1926, pp. 455-459.

251. **ZAWADZKI, J., MORGENSTERN, C. Z., SIBERA, T., AND BRETSZNAJDER, S.** (Reversibility of the Reactions Between Sulfur Dioxide and Calcium Oxide and Between Sulfur and Calcium Oxide.) Roczniki Chem., vol. 12, 1932, pp. 457-467; Chem. Abs., vol. 27, 1933, p. 3873.

252. **ZAWADZKI, J., OSTROUCH, S., AND KWIECINSKI, G.** (Reduction of Sulfur Dioxide by Means of Methane.) Przemysl Chem., vol. 22, 1938, pp. 558-564; Chem. Abs., vol. 33, 1939, col. 3714.

253. **ZEISE, H.** (Homogeneous Gas Equilibria Calculated From Spectroscopic Data.) Ztschr. Elektrochem., vol. 40, 1934, pp. 885-890.

INT.-BU.OF MINES.PGH.,PA. 9269